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Quarterly Report on the Ferrocyanide Safety Program for the Period Ending June 30, 1994

Prepared for the U.S. Department of Energy
Office of Environmental Restoration and
Waste Management

Westinghouse
Hanford Company Richland, Washington

Hanford Operations and Engineering Contractor for the
U.S. Department of Energy under Contract DE-AC06-87RL 10930

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J. E. Meacham
R. J. Cash
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Date Published
July 1994

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QUARTERLY REPORT ON THE FERROCYANIDE SAFETY PROGRAM FOR THE PERIOD ENDING JUNE 30, 1994

J. E. Meacham
R. J. Cash
G. T. Dukelow

ABSTRACT

This is the thirteenth quarterly report on the progress of activities addressing the Ferrocyanide Safety Issue associated with Hanford Site high-level radioactive waste tanks. Progress in the Ferrocyanide Safety Program is reviewed, including work addressing the six parts of Defense Nuclear Facilities Safety Board Recommendation 90-7 (FR 1990). All work activities are described in the revised program plan (Borsheim et al. 1993), and this report follows the same format presented there. A summary of the key events occurring this quarter is presented in Section 1.2. More detailed discussions of progress are located in Sections 3.0 and 4.0.

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LIST OF TERMS

Btu/hr	British Thermal Units per Hour
cal/g	
CASS	Computer Automated Surveillance System
CPAC	Center for Process Analytical Chemistry
DNFSB	Defense Nuclear Facilities Safety Board
DOE	U.S. Department of Energy
DQO	Data Quality Objectives
EIS	Environmental Impact Statement
EA	Environmental Assessment
FAI	Fauske and Associates, Inc.
FTIR	Fourier Transform Infrared
FTIR-PAS	Fourier Transform Infrared-Photoacoustic Spectroscopy
FY	Fiscal Year
g	Gravity
g-mole	Gram-Mole
GAO	U.S. General Accounting Office
IC	Ion Chromatography
IR	Infrared
ISB	Interim Safety Basis
kW	Kilowatt
LANL	Los Alamos National Laboratory
LEL	Lower Explosive Limit
LOW	Liquid Observation Well
M	Mole
NIR	Near Infrared
PNL	Pacific Northwest Laboratory
ppm	Parts Per Million
Rad/h	Rad Per Hour
RSST	Reactive Systems Screening Tool (small adiabatic calorimeter at FAI)
SA	Safety Assessment
SAR	Safety Analysis Report
SD	Supporting Document
SRL	Savannah River Laboratory
SST	Single-Shell Tank
TC	Thermocouple
TMACS	Tank Monitor and Control System
TPA	Tri-Party Agreement, *Hanford Federal Facility Agreement and Consent Order*
USQ	Unreviewed Safety Question
vol%	Volume Percent
VSP	Vent Sizing Package (large adiabatic calorimeter at FAI)
wt%	Weight Percent

1.0 INTRODUCTION

1.1 PURPOSE

This quarterly report provides a status of the activities underway at the Hanford Site on the Ferrocyanide Safety Issue, as requested by the Defense Nuclear Facilities Safety Board (DNFSB) in Recommendation 90-7 (FR 1990). In March 1991, a DNFSB implementation plan (Cash 1991) responding to the six parts of Recommendation 90-7 was prepared and sent to the DNFSB. The implementation plan was updated in fiscal year (FY) 1993 (Borsheim et al. 1992). A revised Ferrocyanide Safety Program Plan addressing the total Ferrocyanide Safety Program, including the six parts of DNFSB Recommendation 90-7, was released in March 1994 (Borsheim et al. 1994). Activities in the revised program plan are underway or have been completed, and the status of each is described in Section 4.0 of this report.

1.2 QUARTERLY HIGHLIGHTS

- Update of the Interim Safety Basis (ISB) document (Wagoner 1993) to incorporate the ferrocyanide safety criteria (Postma et al. 1994) and to reflect closure of the Ferrocyanide Unreviewed Safety Question (USQ) was begun this quarter. Revision of Chapter 6 (Requirements) was completed in May, and a revised topical report (Chapter 5, Section 5) is currently under editorial review and should be distributed by the end of July.

- A close-out report was submitted to the U.S. Department of Energy (DOE) that addresses the 1990 U.S. General Accounting Office (GAO) recommendations on the ferrocyanide hazard (Peach 1990). The report summarizes the progress made on determining the potential for ferrocyanide reactions in Hanford Site high-level waste tanks, and the conditions necessary to sustain an exothermic ferrocyanide reaction. Based on the results obtained by the Ferrocyanide Safety Program, dose consequence calculations and aerosol experiments are considered unwarranted.

- All equipment and safety documentation supporting insertion of instrument trees into assumed leaker tanks were completed this quarter. However, installation activities were stopped because of concern over riser availability for core sampling. After an instrument tree is inserted into a riser, that riser is no longer available for core sampling. Therefore, core sampling may be required before instrument tree installation.

- A report (McLaren 1994) was published this quarter that estimates heat loads for the ferrocyanide tanks expected to have the highest heat loads. The maximum heat load of any ferrocyanide tank is below 4.2 kilowatts (kW), or 14,300 British thermal units per hour (Btu/hr).

- A total of nine ferrocyanide tanks were vapor sampled this quarter. Tank 241-BY-107 had a flammable gas concentration of 3 to 4% of the lower explosive limit (LEL), and tank 241-BY-108 had a concentration of 1% of the LEL. Tanks 241-BY-103, -104, -105, -106, -111, 241-C-109, and -112 had concentrations less than 1% of the LEL. The highest ammonia concentrations where found in tanks 241-BY-107 and -108, at 700 and 97 parts per million (ppm), respectively.

- A report evaluating possible sources of flammable gases, including potential cyclic venting, was completed this quarter (Fowler and Graves 1994). The report concluded that continuous flammable gas monitoring in ferrocyanide tanks is not warranted. The document will be issued for public availability in July 1994.

- Four attempts were made this quarter to obtain push-mode core samples from tanks 241-C-108 and -111. All of the attempts resulted in low core recoveries, less than about 10 volume percent (vol%). Redesign and testing of the push-mode core sampler is now underway in an attempt to improve core recovery. Analyses of a partial sample from tank 241-C-111 yielded similar results to those seen in tanks 241-C-109 and -112 (Simpson et al. 1993a, 1993b). The sample contained 32 weight percent (wt%) water and exhibited an exotherm of -13 calories per gram (cal/g) on a dry basis.

- Neutron detectors from two manufacturers (LND, Inc. and Nancy Woods Laboratory, Inc.) were tested and compared this quarter. The detectors supplied by LND offer the best energy resolution and operate at lower voltages than the Nancy Woods detectors. The Nancy Woods detectors produce a larger average pulse height signal. Tests in radiation fields revealed that all of the detectors could be operated under irradiation. However, the LND detectors were more effective at discriminating against the signal coming from gamma rays.

- The University of Washington's Center for Process Analytical Chemistry completed Phase 2 feasibility work this quarter on near-infrared (NIR) moisture monitoring technology. Experiments showed that particle size and chemical changes in the waste increase the measurement error; however, it is still possible to obtain moisture readings at ± 5 wt% accuracy.

- Examination of results from three different drainage experiments revealed that ferrocyanide waste simulants drain water through a process of consolidation. This is opposite to the behavior of a rigid porous medium, such as sand or saltcake. Direct measurement of the consolidation of actual wastes is recommended to predict the water retention capability of the tank sludge. Centrifuge experiments offer a fast and efficient way to test the hydraulic properties of sludges with only a small sample.

- Since early April, all laboratory work has been halted within radioactive control areas in the 325 Building at Pacific Northwest Laboratory (PNL). The shutdown has affected completion of the work scope outlined in the FY 1994 test plans. Reports will be issued as scheduled in the milestones; however, some of work that was to be completed this FY in the cyanide speciation and cesium solubility tasks will be carried into next FY.

1.3 REPORT FORMAT

Progress of activities under each of the six parts of DNFSB Recommendation 90-7 are arranged in the same order as the program plan (Borsheim et al. 1994). The arrangement also follows the same order provided in Recommendation 90-7. To report on progress, each part of the recommendation is repeated in italics, followed by paragraphs explaining the scope of work on each part or subpart of the recommendation. Subheadings for each task activity report the following:

- Progress During Reporting Period
- Planned Work for Subsequent Months
- Problem Areas and Action Taken
- Milestone Status.

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2.0 BACKGROUND

Various high-level radioactive wastes from defense operations have accumulated at the Hanford Site in underground storage tanks since the mid-1940s. During the 1950s, additional tank storage space was required to support the defense mission. To obtain this additional storage volume within a short time period, and to minimize the need for constructing additional storage tanks, Hanford Site scientists developed a process to scavenge ^{137}Cs from tank waste liquids. In implementing this process, approximately 140 metric tons (154 tons) of ferrocyanide were added to waste that was later routed to some Hanford Site single-shell tanks (SSTs).

Ferrocyanide, in the presence of oxidizing material such as sodium nitrate and/or nitrite, can be made to react exothermically by heating it to high temperatures or by applying an electrical spark of sufficient energy. Under laboratory conditions deliberately created to enhance the potential for reactions, significant exothermic reactions can start as low as 220 °C, but the lowest propagation temperature observed is approximately 250 °C. The reactive nature of ferrocyanide in the presence of an oxidizer has been known for decades, but the conditions under which the compound can undergo endothermic and exothermic reactions have not been thoroughly studied. Because the scavenging process precipitated ferrocyanide from solutions containing nitrate and nitrite, an intimate mixture of ferrocyanides and nitrates and/or nitrites is likely to exist in some regions of the ferrocyanide tanks.

Efforts have been underway since the mid-1980s to evaluate the potential for ferrocyanide reactions in Hanford Site SSTs (Burger 1989, Burger and Scheele 1988). The potential consequences of a postulated ferrocyanide reaction were not evaluated in the safety analyses or safety analysis reports (SARs) applicable to the Hanford Site SSTs. The SAR authors historically have considered a rapid exothermic reaction from fuel/nitrate reactions as an incredible event, and the consequences of incredible events are not required to be analyzed (WHC 1993).

Although not considered a part of the safety analysis for storage of waste in the SSTs, the 1987 Environmental Impact Statement (EIS), *Final Environmental Impact Statement, Disposal of Hanford Defense High-Level Transuranic and Tank Waste, Hanford Site, Richland, Washington* (DOE 1987) did include an environmental impact analysis of potential exothermic reactions involving ferrocyanide-nitrate mixtures. The EIS authors speculated that an explosion could occur during mechanical retrieval of saltcake or sludge from a ferrocyanide waste tank. The EIS authors concluded that this worst-case accident could create enough energy to release radioactive material to the atmosphere through ventilation openings, exposing persons offsite to a short-term radiation dose of approximately 200 millirem. A GAO study (Peach 1990) postulated a greater worst-case accident, with independently calculated doses of one to two orders of magnitude greater than in the EIS. Coupling the ferrocyanide concerns with concerns about high organic concentrations and potential hydrogen accumulations in other Hanford Site high-level waste tanks, the DOE established the High-Level Radioactive Waste Tanks Task Force and Tanks Advisory Panel in August 1990. These two groups were formed to ensure that all safety concerns with high-level waste tanks at DOE sites are identified and addressed in a systematic and timely manner.

The initial focus of the task force and advisory panel was on the Hanford Site Flammable Gas and Ferrocyanide Safety Issues. In September 1990, a special Hanford Site ferrocyanide task team was commissioned by Westinghouse Hanford Company to address all issues involving the ferrocyanide tanks, including the consequences of a potential accident.

The Ferrocyanide Safety Issue is a result of a combination of factors, beginning with the safety studies performed as precursors to using the ferrocyanide scavenging flowsheets. These studies did not address ultimate disposal of the ferrocyanide solids, and were not performed to the conservative standards used today. In addition, no rigorous inventory was kept of the ferrocyanide or other chemicals added to the tanks. Subsequent safety studies determining the risk of adding other chemicals were either not performed, or were performed to less conservative standards. Monitoring systems, such as temperature measurement instrumentation, were allowed to be disconnected and fall into disrepair because the potential hazard was not highlighted.

Although the EIS authors estimated the consequences from a hypothetical explosion, the GAO disagreed with the assumptions used for the dose consequence calculations. Work performed by PNL in 1984-85 (Burger 1989) identified a potential safety problem, but no funding was provided until 1989 to study the Ferrocyanide Safety Issue. An additional issue was subsequently communicated about the assumed radioactive material source term (release fraction) resulting from a hypothetical explosion (Peach 1990).

In October 1990 (Deaton 1990), the Ferrocyanide Safety Issue was declared a USQ[1] because the safety envelope for these tanks was no longer bounded by the existing safety analysis report (Smith 1986). In 1991, using process knowledge, process records, transfer records, and log books, 24 Hanford Site tanks were identified as potentially containing 1,000 gram-moles (g-moles) (465 lb) or more of ferrocyanide [as the $Fe(CN)_6^{4-}$ anion]. These tanks were

[1] An Unreviewed Safety Question, as defined by DOE Orders 5480.5 (DOE 1986) and 5480.21 (DOE 1991), is determined as follows. "A proposed change, test or experiment shall be deemed to involve an USQ if the following apply:

a. The probability of occurrence or the consequences of an accident or malfunction of equipment important to safety, evaluated previously by safety analysis will be significantly increased, or

b. A possibility for an accident or malfunction of a different type than any evaluated previously by safety analysis will be created which could result in significant safety consequences."

placed on a Ferrocyanide Watch List because of the USQ. Re-examination of the historical records (Borsheim and Simpson 1991) indicated that 6 of the 24 tanks do not contain the requisite 1,000 g-moles of ferrocyanide and should not have been included on the Watch List. Four of the 6 tanks were removed from the Watch List in June 1993 (Meacham et al. 1993) and removal of the other two tanks is pending (Borsheim et al. 1993).

The Ferrocyanide USQ was closed on March 1, 1994 by the DOE Assistant Secretary for Environmental Restoration and Waste Management (Sheridan 1994). Closure of the Ferrocyanide USQ was based on safety criteria proposed by Westinghouse Hanford Company and concurred on by outside reviewers and reviewers within DOE. This was the first USQ closure in the current Waste Tank Safety Program since the Watch List was created in 1990.

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3.0 FERROCYANIDE SAFETY DOCUMENTATION

The USQ process depends on an authorization basis that describes those aspects of the facility design basis and operational requirements relied on by DOE to authorize operation. The authorization basis is described in documents such as facility SARs and other safety analyses, hazard classification documents, technical safety requirements, DOE-issued safety evaluation reports, and facility-specific commitments, such as Safety Assessments (SAs) and the ISB (Wagoner 1993). The potential hazards of a ferrocyanide-nitrate/nitrite reaction were discovered to represent an inadequacy in the authorization basis.

A strategy for closing the USQ and resolving the Safety Issue for the ferrocyanide waste tanks was developed by DOE and Westinghouse Hanford Company and presented to the DNFSB in August 1993 (Grumbly 1993). The strategy contains two key steps: (1) developing criteria for safety categories that rank the hazard for each tank, allowing closure of the USQ; and (2) confirmation and final placement of each tank into one of the categories based on core sampling and characterization of the tank contents. The Ferrocyanide USQ was closed on March 1, 1994 by the DOE Assistant Secretary for Environmental Restoration and Waste Management (Sheridan 1994).

Safety and Environmental Assessments. SAs are documents prepared to provide the technical basis to assess the safety of a proposed activity and to provide proper controls to maintain safety. The SA and the accompanying Environmental Assessment (EA) for that operation provide the basis for DOE authorization of the proposed activities. SAs have been approved for vapor space sampling of all ferrocyanide tanks, waste surface sampling, push-mode and rotary-mode core sampling, thermocouple (TC)/instrument tree installation in sound and assumed leaker tanks, and removal of pumpable liquid (interim stabilization).

A generic EA covering all proposed operations in the tank farms has been approved, and a Finding of No Significant Impact was issued by DOE (Gerton 1994). Approval of the generic EA provides adequate National Environmental Policy Act coverage for the planned Ferrocyanide Safety Program activities and streamlines the approval process.

The authorization basis for intrusive tank operations was combined into one document, the ISB, in November 1993 (Wagoner 1993). Safety documentation concerning the ferrocyanide hazard was updated this quarter to reflect the approved ferrocyanide safety criteria and closure of the ferrocyanide USQ. Updates of Chapter 6 (Requirements) of the ISB and the Operating Specifications Document were completed in May. However, revision of Chapter 5, Section 5 (Topical Reports) of the ISB was not completed by the June 24 milestone. Several topical reports, including one for ferrocyanide, are part of the ISB update, and the extent of the update has caused a delay in the review process. The revised topical report is currently under editorial review and should be distributed by the end of July.

Hazard Assessment. The effort to update the ferrocyanide hazards assessment document was redirected in June 1993 toward developing a technical basis document supporting resolution of the Ferrocyanide Safety Issue. An updated ferrocyanide hazards assessment, now referred to as a technical basis document, will not be started until adequate information is available for resolving the Ferrocyanide Safety Issue. Technical information from all Ferrocyanide Safety Program tasks will be incorporated into this document. This document may be necessary to support Safety Issue resolution in FY 1995 for the four Ferrocyanide Watch List tanks in C Farm. Core recovery problems (see Section 4.4.1) may delay Safety Issue resolution for the C Farm tanks. An update of the document may be necessary in FY 1997 to support Safety Issue resolution for the remaining tanks.

Dose Consequences. In September 1990, an Ad Hoc Task Force report recommended that studies be performed to provide information on: (1) the potential for a ferrocyanide-nitrate/nitrite explosion; (2) the conditions necessary in the tanks to initiate an explosion; and (3) the potential consequences of such an occurrence. The GAO advised the Secretary of Energy to implement these recommendations (Peach 1990). A close-out report addressing all three of the GAO recommendations was submitted to DOE this quarter. The report summarizes the progress made on determining the potential for ferrocyanide reactions in Hanford Site ferrocyanide tanks, and the conditions necessary to sustain an exothermic ferrocyanide reaction. Based on the results obtained by the Ferrocyanide Safety Program, dose consequence calculations and aerosol experiments are considered unwarranted.

- **Milestone Status**

  - **January 31, 1994:** Receive DOE approval to close the Ferrocyanide USQ (Safety Initiative 2s). The Ferrocyanide USQ was closed on March 1, 1994 (Sheridan 1994). A letter was sent on March 30, 1994 (Wisness 1994) informing the U.S. Environmental Protection Agency and State of Washington Department of Ecology that Tri-Party Agreement (TPA) milestone M-40-14 (closure of the Ferrocyanide USQ by March 31, 1994) was completed.

  - **June 24, 1994:** Issue an ISB Level 1 report to DOE that provides the safety basis for safe operation of ferrocyanide tanks. Several topical reports contained in the ISB are being updated. This has caused a delay in release of the changes and updating of the ISB should be completed early next quarter.

  - **July 29, 1994:** Issue an update of the ferrocyanide hazards assessment document. This milestone was deferred to FY 1995 and may be canceled if not required to resolve the Safety Issue for the four C Farm tanks.

- **August 31, 1995.** Issue technical basis document supporting Safety Issue resolution for C Farm tanks, if required. Recommend Safety Issue resolution for C Farm tanks. Difficulties in obtaining adequate push-mode core samples from tanks 241-C-108 and -111 may delay completion of this milestone into FY 1996.

- **February 29, 1996.** Obtain DOE approval to remove C Farm tanks from the Watch List. Safety Issue resolved for C Farm tanks. Difficulties in obtaining adequate push-mode core samples from tanks 241-C-108 and -111 may delay completion of this milestone.

- **January 31, 1997.** Revise technical basis document to support Safety Issue resolution for the remaining tanks, if required. Recommend Safety Issue resolution for all tanks.

- **September 30, 1997.** Receive DOE approval to remove all tanks from the Ferrocyanide Watch List. This action resolves the Ferrocyanide Safety Issue.

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4.0 DESCRIPTION OF ACTIVITIES

This section follows the format of the program plan (Borsheim et al. 1994) and describes all work associated with the Ferrocyanide Safety Program. Where applicable, each task activity is described relative to the DNFSB Recommendation (90-7.1 through 90-7.6). The specific recommendation is given, followed by a summary of activities underway to respond to the recommendation (if not already closed out).

4.1 ENHANCED TEMPERATURE MEASUREMENT

"Immediate steps should be taken to add instrumentation as necessary to the SSTs containing ferrocyanide that will establish whether hot spots exist or may develop in the future in the stored waste. The instrumentation should include, as a minimum, additional thermocouple trees. Trees should be introduced at several radial locations in all tanks containing substantial amounts of ferrocyanide, to measure the temperature as a function of elevation at these radii. The use of infrared techniques to survey the surface of waste in tanks should continue to be investigated as a priority matter, and on the assumption that this method will be found valuable, monitors based on it should be installed now in the ferrocyanide bearing tanks."

4.1.1 Instrument Trees

Work in several areas has developed a broader knowledge base and has warranted several changes in the approach to implementing this recommendation. Originally, it was planned to add several temperature measurement instruments to each tank. This plan has been modified to ensure that there is at least one instrument tree with replaceable TCs in each ferrocyanide tank. Additionally, there should be at least two operational temperature-sensing elements in the waste to ensure a true temperature measurement, and one or more in the vapor space.

The new data that have warranted this action include: (1) many of the TC elements in the existing trees have been returned to service and measured temperatures are as expected; (2) thermal modeling to date (McLaren 1994) and an enhanced process knowledge show that the waste is relatively homogeneous horizontally with respect to heat generation (thus a hot spot is most likely improbable); (3) any reasonable number of instrument trees would not be likely to detect a hot spot; and (4) new estimates of tank heat content based on tank temperatures show lower values than previous estimates.

When completed, the results will be two instrument trees in all but three ferrocyanide tanks (241-BY-106, -111 and -112). Tank 241-BY-106 already contains an instrument tree with replaceable TC elements. Tanks 241-BY-111 and -112 had no operable instrument tree, and the waste temperatures were measured via a dedicated TC element installed in each tank's LOW. New instrument trees with replaceable temperature-sensing elements have now been installed in these two tanks. The existing instrument trees in the tanks will be monitored as well as the newly installed trees. It is expected that the older trees will eventually fail in a manner such that they cannot be repaired, and they will not be replaced.

- **Progress During Reporting Period.** Five instrument trees with heated vapor sampling tubes have been fabricated for insertion into assumed leaker ferrocyanide tanks. All equipment and safety documentation supporting insertion of the trees were completed this quarter. An instrument tree was installed in tank 241-BY-107 in April.

  Installation of the instrument trees in the remaining assumed leaker tanks has been delayed because of concern about riser availability for core sampling. Once an instrument tree is inserted into a riser, that riser is no longer available for core sampling. Therefore, it is necessary that core sampling be performed before installation of an instrument tree. However, core sampling and instrument tree installation schedules have not been finalized, and a decision to require core sampling first is still pending.

  A survey of available risers in the ferrocyanide tanks was begun this quarter. The riser inspection includes a historical review of instrumentation occupying risers in the tanks, and physical inspection of the available risers for potential blockage that may obstruct core sampling activities.

  Installation of TC trees into 241-BX-102 has been delayed, because DOE approval to remove this tank from the Ferrocyanide Watch List is pending and installation of trees into tanks on the Watch List is given higher priority.

- **Planned Work for Subsequent Months.** Instrument trees will be installed into the remaining assumed leaker tanks, probably after characterization is complete. Additional instrument trees will be fabricated.

  The survey of available risers for core sampling and instrument tree installation will be completed.

- **Problem Areas and Action Taken.** Installation of instrument trees has been delayed pending decisions on whether characterization will be performed first. A riser survey is being conducted to determine the number of risers available for characterization and instrument tree installation.

- **Milestone Status.**

  - **September 30, 1994**: Install nine instrument trees into assumed leaker ferrocyanide tanks. The number of instrument trees installed will be only eight, because there are currently only eight remaining ferrocyanide tanks (including 241-BX-102, which is pending removal) that require instrument trees. This milestone also addresses the September 1994 TPA milestone (M-40-02B), installation and operation of six instrument trees in ferrocyanide tanks. This milestone is behind schedule. Once new core sampling and instrument tree installation schedules are finalized, this milestone will be rescheduled.

- **September 30, 1994**: Develop criteria for upgraded temperature monitoring capabilities in ferrocyanide tanks (TPA milestone M-40-02A). This milestone is on schedule. A draft of this report was submitted to the Washington State Department of Ecology for review in April.

- **December 31, 1994**: Complete installation of instrument trees in assumed leaker tanks. Replace temperature-sensing elements in the remaining two ferrocyanide tanks (241-BY-105 and -106) as necessary. Completion of this milestone will be delayed as discussed above: completion is now expected before September 1995.

4.1.2 Upgrades to Existing Temperature Monitoring Instrumentation

This task determined the operability and accuracy of previously installed TC elements in the original 24 Ferrocyanide Watch List tanks. The original and newly installed instrument trees provide temperature measurements for the ferrocyanide tanks.

Field measurements were taken in 1991 on each TC element in the then-existing trees to determine the resistance and voltage across the junction and across each lead to ground. The exact condition of each TC was determined by resistance and voltage measurements (Bussell 1992). This work was completed in FY 1991 with a total of 265 TCs being evaluated. Work in FY 1992 focused on repair and recovery of 92 TCs that were found to be failed or marginal in performance. This task was completed in FY 1992.

- **Progress During Reporting Period.** No progress was required or planned.

- **Planned Work for Subsequent Months.** None.

- **Problem Areas and Actions Taken.** None.

- **Milestone Status.** This task is complete.

4.1.3 Hot Spot Thermal Modeling

Radioactive materials decaying in Hanford Site waste tanks generate heat. A concern, raised when the ferrocyanide tanks first became a safety issue, has been whether an exothermic excursion and local propagation could occur within the ferrocyanide waste if a sufficient concentration of ferrocyanide and a high enough temperature were present. There are usually only one or two instrument trees in each ferrocyanide tank, and the trees are not always at the same location. Consequently, it is questionable whether abnormal heat generation could exist in these tanks and not be detected. This task models and analyzes the available temperature data from the ferrocyanide tanks in order to determine the heat load and temperatures as a function of depth and radial location. Sensitivity and parametric analyses are included to determine the magnitude of hot spots that would have to exist within the waste to reach propagation temperatures.

State-of-the-art validated computer codes are used in the modeling. They are benchmarked with existing data and employ two- and three-dimensional capabilities. Both steady-state and transient models are used. The intent of this work is to determine accurate heat loads for each ferrocyanide tank and to model hypothetical hot spots.

- **Progress During the Reporting Period.** Analyses of tanks 241-BY-103, -105, -106, -107, -108, -110, -111, and 241-C-109 for heat load and thermal characteristics was completed and a report of the results released this quarter (McLaren 1994). The BY tanks have the highest anticipated heat loads (see Table A-1 in Appendix A) of the tanks on the Ferrocyanide Watch List (Crowe et al. 1993). Several refinements were incorporated from the original analyses, including transient solutions and thermal conductivity measurements of the soil surrounding the ferrocyanide tanks. Upper and lower limits for the estimated heat loads are presented in the report. The maximum heat load of any ferrocyanide tank is below 4.2 kW (14,300 Btu/hr).

- **Planned Work for Subsequent Months.** The updated thermal heat transfer/heat load model will be used to analyze the heat load and thermal characteristics of the remaining Ferrocyanide Watch List tanks. The report on the remaining analyses will be prepared and issued later in FY 1994.

  The scope of the dryout position paper has been expanded to include discussion on additional dryout mechanisms and the experiments that provide the bases for these discussions. The revised dryout position paper will be completed and released next quarter.

- **Problem Areas and Action Taken.** None.

- **Milestone Status.**

  - **May 31, 1994.** Complete additional analyses and issue an update of the report *Ferrocyanide Safety Program: Credibility of Drying out Ferrocyanide Waste by Hot Spots* (Dickinson et al. 1993), approved for public release. This effort was extended to the end of FY 1994 to include discussion of additional dryout mechanisms and the results of experiments that provide the bases for the discussions.

- **June 30, 1994.** Complete thermal hydraulic analyses of heat loads for eight ferrocyanide tanks (241-BY-103, -105, -106, -107, -108, -110, -111, and 241-C-109) and issue a report available to the public. This report was issued on schedule (McLaren 1994).

- **September 30, 1994.** Complete thermal hydraulic analyses of heat loads for all remaining ferrocyanide tanks and issue a report available to the public. This milestone remains on schedule.

4.1.4 Infrared Scanning System

Infrared (IR) scanning systems are commercially available from numerous vendors. These systems are sensitive to changes of ±0.3 °C or less under ideal conditions, and offer promise for mapping surface temperature profiles in the ferrocyanide tanks. Thermal modeling performed on ferrocyanide tank 241-BY-104 suggested that if hot spots with temperatures of concern are possible, surface temperature differences might be great enough to be detected by infrared mapping.

A position paper on the credibility of hot spots and the need for further IR scanning was completed and issued in April 1993 (Dickinson et al. 1993). This paper examined potential concentration mechanisms and determined the degree of concentration required to produce temperatures high enough to dry the ferrocyanide waste. The paper concluded that such concentrations were incredible. Based on this report, Westinghouse Hanford Company recommended that no further planning be pursued for IR scans for the purpose of detecting hot spots.

- **Progress During the Reporting Period.** None.

- **Planned Work for Subsequent Months.** A draft report on the infrared scans of tank 241-S-110, *Application of Infrared Imaging in Ferrocyanide Tanks*, (WHC-EP-0593) was submitted to DOE in January 1993. Approval to release this report for public availability is pending.

- **Problem Areas and Action Taken.** None.

- **Milestone Status.** None.

4.2 CONTINUOUS TEMPERATURE MONITORING

"The temperature sensors referred to above [Recommendation 90-7.1] should have continuous recorded readouts and alarms that would signal at a permanently manned location any abnormally high temperatures and any failed temperature instrumentation."

This task provides continuous monitoring of presently installed (and operable) TCs for the ferrocyanide tanks. New instrument trees will be connected to the system as they are installed into each tank, resulting in continuous monitoring of temperature in the ferrocyanide tanks. All data are collected automatically at the continuously manned Computer Automated Surveillance System (CASS) Operator Control Station. The monitoring system is independent of the CASS and capable of displaying data to an operator on request. Trend data on selected points are available for display in numeric or graphic form.

The system, which became operational in September 1991, has the capacity to assign alarms for a change in the value of any temperature point. Alarms, if they occur, trigger an audible annunciator and are logged immediately to hard copy. An alarm summary display provides a list of the most recent alarms in order of occurrence. Each alarm can be identified by point and time of occurrence. Operator acknowledgement of the alarm will silence the audible annunciator. Signal conditioning and multiplexing are performed locally at each tank. This eliminates the need to transmit low-level signals to the tank farm boundary and reduces cable runs. Electronic noise, extension wire corrosion, and thermal gradients are also reduced.

- **Progress During Reporting Period.** Construction was completed for BX, C, and T Tank Farms this quarter. All ferrocyanide tanks with TCs are now connected to the Tank Monitor and Control System (TMACS) for temperature monitoring with the exception of some of the new trees installed in FY 1993 and FY 1994. Temperatures are being monitored on a continuous basis.

- **Planned Work For Subsequent Months.** Connection of new instrument trees to TMACS will be made as soon as practical after the trees are installed.

- **Problem Areas and Action Taken.** None.

- **Milestone Status.**

  - **September 30, 1994.** Complete installation of TMACS for the four ferrocyanide tanks in C Farm, one tank in T Farm, and two tanks in BX Farm. Ferrocyanide tanks removed from the Watch List (241-BX-110, 241-BY-101, and 241-T-101), or pending removal (241-BX-102 and -106) from the Ferrocyanide Watch List, will be connected in FY 1995. This milestone was completed this quarter.

- **December 31, 1994.** Complete installation of TMACS for new instrument trees installed in FY 1994. The completion of TMACS installations is also a TPA milestone (M-40-02). This milestone is behind schedule.

4.3 COVER GAS MODELING

"Instrumentation should also be installed to monitor the composition of cover gas in the tanks, to establish if flammable gas is present."

4.3.1 Interim Flammable Gas Monitoring

The effort to conduct flammable and toxic gas monitoring and analyses in the ferrocyanide tanks is continuing. Most of this effort was transferred to the Tank Vapor Issue Resolution Program, which is coordinating interim gas monitoring of the ferrocyanide tanks, as well as those tanks involved with the tank vapor safety issue. Tank vapor spaces are measured for flammability using a commercial combustible gas monitor (calibrated with pentane gas), and are monitored for potential toxic gases using an organic vapor monitor and Dräger[2] tubes as required by the safety assessment and work procedures for a particular activity. Development and validation of alternative technologies for vapor space characterization are in progress using SUMMA[3] canisters and specific absorption (Dräger™) tubes. The initial vapor space sampling was done in several tank locations (i.e., from two widely separated risers) and at three elevations in the vapor space. Review of the sample data indicated that sampling from one riser was adequate; the number of sample elevations may be reduced in the future.

- **Progress During Reporting Period.** Nine ferrocyanide tanks were vapor sampled this quarter, 241-BY-103, -104, -105, -106, -107, -108, -111, 241-C-109, and -112. Tank 241-BY-107 had a flammable gas concentration of 3 to 4% of the LEL and tank 241-BY-108 had a concentration of 1% of the LEL. The remaining tanks contained less than 1% of the LEL. The highest ammonia concentrations were also found in tanks 241-BY-107, and -108, approximately 700 and 97 ppm, respectively. Table A-2 in Appendix A provides gas analyses for the ferrocyanide tanks sampled to date.

- **Planned Work For Subsequent Months.** Flammable gas sampling and selected noxious gas monitoring will continue, as required, to support planned core sampling and instrument tree installation.

- **Problem Areas and Actions Taken.** None.

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[2]Trademark of Drägerwerk Aktiengesellschaft, Inc., Lubeck, Germany.

[3]Trademark of Molectrics, Inc., Cleveland, Ohio.

- **Milestone Status**

  - **September 30, 1994.** Complete vapor space sampling of remaining ferrocyanide tanks, as required, to support various field activities. This milestone remains on schedule.

  - **September 30, 1995.** Complete vapor space sampling of remaining ferrocyanide tanks. This milestone addresses the November 1995 TPA milestone M-40-03.

4.3.2 Continuous Gas Monitoring

Options for installing a gas monitoring capability on new instrument trees were reviewed and a heated vapor sampling tube was added to the design of the remaining instrument trees to be installed in ferrocyanide tanks. These modifications will allow vapor space sampling on a continuous or intermittent basis. The first instrument tree incorporating the new design was installed in tank 241-BY-107 in April 1994. The need for continuous gas monitoring is being addressed in a study that also assesses the potential for cyclic venting and the possibility of accumulating flammable gases.

The possibility that localized concentrations or stratification of gases exist in the tanks has been evaluated. A modeling study to determine airflow patterns in the vapor space of tank 241-C-109 was conducted to evaluate the amount of mixing and the local gas concentrations that could occur. The study revealed that the gases in the tank are well mixed and follow Graham's law for gaseous diffusion; therefore, an analysis of a second tank was considered unnecessary because of the well-mixed environment calculated for 241-C-109 (Wood 1993).

- **Progress During Reporting Period.** A report evaluating possible sources of flammable gases, including potential cyclic venting, was prepared this quarter (Fowler and Graves 1994). The report concluded that continuous flammable gas monitoring in ferrocyanide tanks is not warranted based on: (1) the low concentration of flammable gases found to date; (2) anticipated low ferrocyanide concentrations because of waste aging; (3) analytical results from tanks 241-C-109 and -112 showing that the fuel concentration in the tanks is not as high as postulated by flowsheet values and operating records; and (4) calculations of hydrogen generation using realistic generation values and passive ventilation assumptions. The report will be released for public availability early next quarter.

- **Planned Work For Subsequent Months.** Pending DOE review, no further work is planned in this area.

- **Problem Areas and Actions Taken.** None.

- **Milestone Status.**

  - **March 31, 1994**: Complete an evaluation report to determine which gases, if any, need to be continuously monitored in selected ferrocyanide tanks. A report was completed this quarter (Fowler and Graves 1994) and will be cleared and issued in July 1994.

  - **September 30, 1995**: Develop and design continuous monitoring equipment, if required.

  - **September 30, 1997**: Install continuous gas monitoring equipment in six tanks, if required.

4.3.3 Tank Pressure Monitoring

Public Law 101-510 (1990) (Section 3137 - also known as the Wyden Amendment) requires that "*... the Secretary of Energy shall identify which single-shell tanks [Watch List]... may have a serious potential for release of high-level waste due to uncontrolled increases of ... pressure. After completing such identification, the Secretary shall determine whether continuous monitoring is being carried out to detect a release or excessive ... pressure at each tank so identified. If such monitoring is not being carried out, as soon as practicable the Secretary shall install such monitoring....*"

The ferrocyanide tanks were initially identified as having "a serious potential for release" and were placed on the Watch List; however, pressure monitoring capability does not presently exist for the tanks. It would take several years for pressure monitoring instrumentation to be installed and connected to a continuously manned location, because of the capital project time cycle. Sufficient knowledge on the safety of the Ferrocyanide Watch List tanks exists at this time such that the USQ has been closed (see Section 4.0). Because of waste aging, it is very likely that all of the ferrocyanide tanks now contain less than the 8 wt% sodium nickel ferrocyanide specified in the fuel criterion for the SAFE category (see also Postma et al. 1994). It is anticipated that characterization (core sampling and data interpretation) will place all of the tanks into the SAFE category, because of the low fuel value remaining. Placement of the tanks into the SAFE category means the tanks are candidates for removal from the Ferrocyanide Watch List. This would eliminate the need for continuous pressure monitoring for off-gases from a ferrocyanide reaction.

- **Progress During Reporting Period.** A summary of the rationale for not installing pressure monitors in ferrocyanide tanks is presently being prepared. Low gas generation rates (Fowler and Graves 1994), and the low potential for exothermic ferrocyanide reactions (Postma et al. 1994) indicate that continuous pressure monitoring is not warranted.

- **Planned Work For Subsequent Months.** Complete summary of the rationale for not installing pressure monitoring in ferrocyanide tanks, and submit recommendations to DOE.

- **Milestone Status.**

  - **July 29, 1994.** Complete studies to determine whether continuous pressure monitoring is required for some or all ferrocyanide tanks. This milestone remains on schedule.

  - **September 30, 1995.** Install the first phase of pressure monitoring instrumentation, if required.

  - **September 30, 1996.** Install pressure monitoring instrumentation and readout capability on all applicable ferrocyanide tanks, if required.

4.4 FERROCYANIDE WASTE CHARACTERIZATION

"The program of sampling the contents of these tanks should be greatly accelerated. The proposed schedule whereby analysis of two core samples from each single-shell tank is to be completed by September 1998 is seriously inadequate in light of the uncertainties as to safety of these tanks. Furthermore, additional samples are required at several radii and at a range of elevations for the tanks containing substantial amounts of ferrocyanide."

Characterization of the waste in the ferrocyanide tanks is necessary to: (1) guide further chemical reaction studies with the ferrocyanide waste simulants; (2) determine actual waste chemical and physical properties; (3) determine how the ferrocyanide waste can be safely stored *in situ*, and classify the tanks by safety category accordingly, until retrieval and disposal actions are completed; and (4) apply the study results to the final remediation of the waste. This information is necessary to resolve the Ferrocyanide Safety Issue.

The important reactive materials present in the ferrocyanide tanks are fuel (ferrocyanides, sulfides, and reduced carbon species such as organic complexants), oxidants (nitrates and nitrites), and inerts or diluents (including phosphates, aluminates, sulfates, carbonates, oxides, and hydroxides). The location of fission products such as ^{137}Cs and ^{90}Sr is important because these products are heat sources and potential source terms in postulated radiological releases from a hypothetical ferrocyanide reaction. The water content of the waste is very important because water's high heat capacity and vaporization heat make it an effective inerting material. Water can prevent a sustained combustion or a propagating reaction; wet ferrocyanide material would require drying before it could react or propagate.

4.4.1 Core Sampling and Analyses

Core Sampling. Both rotary-mode and push-mode core sampling capabilities will be used to obtain core samples from the Watch List tanks. Tanks without saltcake and with relatively soft waste solids can be core sampled by the push-mode method. If a hard saltcake layer is present, rotary-mode core sampling will be used. The first ferrocyanide tank scheduled for rotary-mode core sampling is 241-BY-106.

Each core consists of several 48-cm (19-in.) segments (or portions thereof) depending on the depth of the waste in the tank. The sludge layer in these cores will be divided into four 12-cm (4.75-in.) subsegments for each 48-cm segment. If the tank contains a saltcake layer, the saltcake segments will be divided into only two subsegments. Process flowsheet knowledge, tank historical data, and results obtained from tests with ferrocyanide sludge simulants are used to supplement the analytical results from core sampling.

The priority for sampling ferrocyanide tanks has been changed to reflect the need to determine the reactive properties of the contents. In response to DNFSB Recommendation 93-5 to expedite sampling and analyses required to address safety issues in the Hanford Site Watch List tanks, the analysis plans for future ferrocyanide tank core samples (and the plans for other Watch List tanks) have been revised. The Watch List tanks have been given priority for core sampling, and the number of required analytes was reduced and refocused on safety-related properties.

- **Progress During Reporting Period.** A total of four attempts were made this quarter to push-mode core sample tanks 241-C-108 and -111. All of the attempts resulted in low core recoveries. Core samples 58, 59, and 60 from tank 241-C-111 contained 26.5 grams (~3.8 cm [1.5 in.] of an anticipated 23 cm [9 in.]), 1.7 grams (anticipated 20 cm [8 in.]), and 19.7 grams (~2.5 cm [1 in.] of an anticipated 15 cm [6 in.]) of material, respectively. Similarly, core recovery for tank 241-C-108 was less than 20 grams (~2.5 cm [1 in.]).

  Although core recovery was not adequate to divide the samples into quarter segments, some analyses were performed on cores 58 and 59. Core 58 contained a small rock, with a mass of approximately 8 grams. The remaining sample contained 32 wt% water and an exotherm of -13 cal/g (on a dry basis). Core 59 contained 1.7 grams of off-white, crust-like material. This sample contained no exotherm and is believed to be composed primarily of aluminum hydroxide. Core 60 was archived and no analyses are planned for this sample at this time. Results from limited analyses of the 20 grams of material from tank 241-C-108 are pending.

  Because of poor recovery during push-mode core sampling, the sampler design is being modified and tested. Testing on simulants revealed poor recovery when the surface material is considerably harder than the material beneath it. Parameters being tested include drill bit design, hand rotation of the sampler, velocity of the sampler through the waste, and impact of the sampler with the waste surface. In-tank testing of the sampler should be completed next quarter.

While testing of the push-mode core sampler is being conducted, tank 241-C-111 will be auger sampled. Because the safety criteria are applied on a quarter segment basis (i.e., 12-cm [[4.75-in.] layers), samples will be taken in successive 12-cm increments. The auger shroud will be left in place and the auger will be dropped down the same hole during each sampling. Observations of waste extracted during push-mode sampling suggest the waste in this tank is rigid, and will not readily slump into the hole created by the auger.

- **Planned Work For Subsequent Months.** When redesign and testing of the push-mode core sampler is completed, tank 241-C-108 will be re-sampled. Rotary-mode core sampling of the first ferrocyanide tank (241-BY-106) has been tentatively re-scheduled for September. Access to one of the risers in Tank 241-BY-104 requires construction of an elevated ramp for the rotary-mode truck. This ramp will not be available until early next FY. Rotary-mode sampling was originally scheduled for completion in May.

  The data interpretation report for tank 241-T-107 will be completed in August 1994. The ferrocyanide Data Quality Objectives (DQO) document (Buck et al. 1993) has been updated and will be re-released next quarter as a Westinghouse Hanford Company Supporting Document (SD). Because the DQO report is a living document and may receive several revisions, the SD format allows the Hanford analytical laboratories to quickly retrieve the most current version for their use.

- **Problem Areas and Actions Taken.** Push-mode sampling of ferrocyanide tanks 241-C-108 and -111 resulted in poor core recovery. As a result, the push-mode sampler is being re-designed and tested. An in-tank test should be completed next quarter. While design and testing are being conducted, auger samples will be taken in tank 241-C-111.

- **Milestone Status.**

  - **February 28, 1994:** Complete interpretation of ferrocyanide tank 241-T-107 analytical data and issue a report cleared for public release. This milestone was deferred to August 15, 1994, because of difficulty in interpreting the limited data from core samples with low recovery.

  - **September 30, 1994:** Obtain full-length push-mode core samples from two ferrocyanide tanks (241-C-111 and -C-108). This milestone may be delayed because of the problems encountered with push-mode core sampling of these tanks.

- **September 30, 1994**: Obtain full-length rotary-mode core samples from three ferrocyanide tanks (241-BY-106, -105, and -108). Completion of this milestone has slipped approximately three months because the rotary-mode core sampler was not ready in April as originally planned. Tank 241-BY-106 will be sampled first (rather than 241-BY-104) in September 1994.

- **September 30, 1995**: Obtain full-length rotary-mode core samples from the remaining ferrocyanide tanks.

- **March 31, 1995**: Complete data interpretation reports, for public release, for five ferrocyanide tanks (241-C-108, -111, 241-BY-106, -105, and -108). Completion of this milestone has slipped because of delays in obtaining core samples. A new date will be set after successful operation of the rotary-mode core sampling truck.

- **June 28, 1996**: Complete data interpretation reports, available for public release, for the remaining ferrocyanide tanks.

Fourier Transform Infrared Spectroscopy Analyses. Fourier Transform Infrared (FTIR) spectroscopy is rapidly becoming the method of choice for demanding applications such as *in situ* and remote characterization of highly toxic and hazardous materials. Recent developments in FTIR-based fiber optic spectroscopy have provided a new methodology to chemically characterize ferrocyanide-bearing waste. Chemometrics and microprocessors that allow storage and rapid analyses of data have significantly contributed to the development of state-of-the-art fiber optic probes.

- **Progress During Reporting Period.** Some of the Fourier transform infrared-photoacoustic spectroscopic (FTIR-PAS) technology developed at the Ames Laboratory, Iowa State University, was transferred to Westinghouse Hanford Company this quarter. To facilitate this technology transfer, similar instrumentation (FTIR-PAS spectrometer and photoacoustic cell) has been purchased by the 222S Laboratory. The FTIR system is capable of sample examination from the far infrared to the ultraviolet regions of the light spectrum. It can also perform in-scan co-addition with scanning rates of 25 to 800 hertz.

  During this initial phase of technology transfer, collection and treatment of the spectral data were performed using the FTIR vendor's software. However, Ames Laboratory has developed a rapid and automated method for the simultaneous determination of sulfates, phosphates, and nitrates. Work on the software to measure the ferrocyanide content is in progress.

- **Planned Work For Subsequent Months.** Develop ferrocyanide analytical software and complete technology transfer from Ames Laboratory.

- **Problem Areas and Actions Taken.** None.

- **Milestone Status.**

  - **July 30, 1994:** Provide an interim letter report on the status of FTIR system performance in analyzing simulants and actual waste material. This task is on schedule.

  - **September 30, 1994:** Issue a publicly available progress report on FY 1994 FTIR work with recommendations on future work. This milestone is on schedule.

  - **September 30, 1995:** Issue a final report on FTIR technology development and demonstration, if warranted.

  - **September 30, 1996:** Deploy an *in situ* FTIR system, if warranted.

4.4.2 Estimation of Moisture Content

Methods for determining moisture concentrations in ferrocyanide waste tanks are being developed using data analysis and available surveillance systems. Two *in situ* moisture monitoring technologies are currently being investigated by the Ferrocyanide Safety Program: neutron diffusion and NIR spectroscopy. Additional moisture monitoring technologies, such as copper foil activation, phase change thermal measurements, electrical conductivity, and time domain reflectometry, are being evaluated by other programs.

Neutron Diffusion. Well-logging techniques, coupled with computer modeling, are being applied to neutron diffusion technology to determine information about moisture levels, material interfaces, and other waste characteristics in the ferrocyanide tanks. Development of an improved neutron-diffusion-based detector system began this FY. This improved technique would primarily be used to determine the axial moisture concentration profile within the ferrocyanide tanks.

Moisture measurement using neutron diffusion is an established technology. The technique uses a neutron source and one or more neutron detectors. The thermal neutrons reaching a detector originate as fast neutrons from the source and are slowed or absorbed by the medium. Because hydrogen atoms are very effective at slowing down neutrons, the detector response is a strong function of the surrounding moisture concentration.

Two methods are generally used in the measurement of moisture concentration around wells using neutron diffusion. The first method, the moisture gauge, has a short source-to-detector spacing on the order of 0 (the source is placed in a ring around the detector) to 6 cm [2 in.]. The response of a moisture gauge is characterized by an increase in detector response with increasing moisture concentration of the surrounding medium. The second method, the neutron log, often has two detectors with longer source-to-detector spacings (20 to 50 cm [8 to 20 in.]). The detectors in a neutron log arrangement exhibit a decreased response to increased moisture concentrations. The detector placed at the shorter spacing is used to correct the response of the longer-spaced detector for borehole effects.

The source-to-detector spacing of the existing probe may be adjusted with the addition of a source extender. Computer modeling of the existing neutron probe system revealed that, in its current configuration, it responds most like a moisture gauge. The probe will operate as a neutron log with the addition of a source extender.

- **Progress During Reporting Period.** Neutron detectors from two manufacturers (LND, Inc. and Nancy Woods Laboratory, Inc.) were tested and compared this quarter using a Cf-252 neutron source. The alpha-particle energy resolution and optimum operating voltages were determined for the probes. The detectors supplied by LND offered the best energy resolution and operate at lower voltages than the Nancy Woods detectors. The Nancy Woods detectors produced a larger average pulse height signal.

  The detectors were subjected to gamma ray fields comparable to those expected in the ferrocyanide tanks. An Ir-192 gamma source was used to provide gamma exposure rates of up to about 360 Rad per hour (Rad/h) on the probe housing containing the detector. All of the detectors were operable in this radiation background; however, the LND detectors seemed to be more effective at discriminating against the signal coming from gamma rays.

  Thermoluminescent dosimeters were lowered into the liquid observation wells (LOWs) of three ferrocyanide tanks (241-BY-104, -110, and 241-TX-118) to measure the ambient gamma dose rates. The maximum measured gamma dose rate was 379 Rad/h, but the typical dose rate in most of the waste was between 50 and 150 Rad/h.

  Preparation of a neutronically equivalent simulant containing 25 wt% water (all chemically bound to the constituent compounds) was completed this quarter. The water content and uniformity throughout the simulant is more easily controlled and maintained by using compounds with bound water. This moisture standard will be used to help complete moisture response calibrations using the new neutron probes.

- **Planned Work for Subsequent Months.** Final tests will be performed on the completed neutron probe prototypes. These tests will include moisture response calibrations with known-moisture-content ferrocyanide waste simulants. Two additional moisture simulants will be prepared containing about 15 and 20 wt% water. Computer modeling will be performed to compare calculated predictions with the measurements. These same computer models will then be adapted to perform tank waste modeling. Results of the tank waste modeling will assist with interpretations of prototype tank scans yet to be performed. Initial test scans of ferrocyanide tanks using the prototype probes are expected to begin in July 1994.

- **Problem Areas and Action Taken.** The potential existence of material anomalies near the LOW, such as air gaps between the LOW and surrounding waste materials, will affect moisture measurements from within the LOW. Better ways of identifying anomalies and methods to correct moisture measurements for anomalies continue to be investigated. Neutron probes will be tested in simulants duplicating some of the potential anomalies. Modeling and testing will be combined to produce a computer code that will automatically process the data to give a best estimate of the waste moisture concentration.

- **Milestone Status.**

  - **September 30, 1994:** Provide a documented working prototype neutron probe system for moisture monitoring.

  - **September 30, 1995:** Complete installation and deployment of the first phase of the neutron moisture monitoring system and initiate monitoring.

  - **September 30, 1996:** Complete installation and deployment of the neutron moisture monitoring system for routine monitoring in ferrocyanide tanks.

Near Infrared Spectroscopy. Infrared spectroscopy of samples containing water is normally dominated by strong absorption from the water molecules. The strength of this absorption is sufficient to determine the water content from the back-scattered light from the surface. In this application, the near infrared 1.4 to 1.5 x 10^{-6}-m region is being investigated for moisture determination in tank waste materials. This optical band, in addition to having a strong sensitivity to water, can be instrumented with conventional optical fibers, windows, and lens components.

For waste tank applications, two methods of implementing NIR absorption are being investigated. Both approaches use back-scattered NIR energy and wavelength processing to extract moisture data. The first method uses an NIR spectroscopy system with a remote fiber optic probe that makes a point moisture measurement. This system could be deployed by a cone penetrometer or surface scanning arm, such as the light-duty utility arm being developed for early *in situ* tank investigations. Deployment as a contact or non-contact sensor is possible since window and lens components are available for the NIR optical region. The second implementation method being investigated is a non-contact remote camera with a sensitive NIR detector and powerful NIR source that will measure moisture of a point from a large lift-off distance. By scanning this point over the waste surface, moisture data can be obtained, in much the same way that temperature contours are obtained using thermal cameras.

A contract is in place with the University of Washington's Center for Process Analytical Chemistry (CPAC) to study infrared spectroscopy as a tool for *in situ* moisture monitoring. Phase 1 of the study evaluated potential characterization using several light frequencies (visible, NIR, and mid-infrared) and concluded that NIR possessed the greatest potential (Reich and Veltkamp 1993).

- **Progress During Reporting Period.** CPAC completed Phase 2 work on NIR moisture monitoring technology this quarter. This study showed that for a tank-scale demonstration of the remote, non-contact camera concept, there is adequate sensitivity to consider a non-contact, camera-type moisture sensing system. However, initial atmospheric absorption analysis indicated that the absorption by the vapor space moisture will strongly impact any type of "open-path" moisture measurement. Absorption is a function of the volume of water encountered by an optical beam. This is a function of both the relative humidity (water concentration) and the path length in the vapor space area. Moisture sensing with fiber optic probes does not have this sensitivity because the "free" optical path lengths are insignificant (on the order of 2.5 to 5.0 cm (1 to 2 in.), versus 3 to 46 m for the "open path" concept). Additional studies are in progress to quantify the potential impact on sensing accuracy and to identify possible concepts for mitigation of this interference.

  The Phase 2 CPAC work (Reich and Veltkamp 1994) also showed that particle size and chemical changes in the waste increase the measurement error, but it is still possible to obtain moisture readings within a $\pm$ 5 wt% accuracy envelope using the reflectance spectrum. If these interferences are part of the test data used to develop the partial least squares calibration, CPAC has shown that the error envelope is smaller.

  Software and system hardware problems have slowed testing of the Savannah River Laboratory (SRL) NIR moisture system. Malfunctioning hardware components have prohibited system operation, while errors in software have impacted the ability to acquire good spectra, and are preventing the system from being calibrated and tested. This will delay, by approximately two months, transferring the SRL NIR system to the hot cell for testing. Initial testing has indicated that the original calibration was limited to a 0 to 24 wt% moisture content, which is not adequate for the range anticipated for actual waste samples.

- **Planned Work for Subsequent Months.** Operational documentation for the SRL system will be completed to support cold and hot cell system operation. The calibration and testing of the NIR system with pure materials and simulants will be completed. Based on these test results, a decision will be made on the status of the NIR and its potential ability to be used for the hot cell testing of archived waste tank materials. CPAC will complete a Phase 3 work scope to investigate the NIR moisture performance of T Plant simulants. Concepts for mitigating the absorption from the moisture in the tank vapor space will also be identified.

- **Problem Areas and Action Taken.** To accelerate cold and hot testing, a second SRL NIR spectroscopy system has been obtained. System operating documentation is being prepared to support the future operation of this measurement system, and some spare system components have been purchased.

  Moisture in the tank vapor space is a strong interference for using "open-path" NIR moisture sensing concepts in the tanks. Fiber optic probe systems are not affected by this because of their short "free" path lengths. However, with the "open-path" camera concepts the optical path in the vapor space can approach 46 m. With high moisture levels (over 50% relative humidity), the attenuation of an NIR optical beam crossing the tank vapor space is significant in comparison with the changes in surface reflectance. Potential concepts for mitigating this absorption are being investigated before proceeding with a scale-up demonstration.

- **Milestone Status.**

  - **March 31, 1994:** Complete the Phase 2 surface monitoring interference study/scale up report. Work on this milestone was completed this quarter, and will be reported in two separate documents. The first of these reports (Reich and Veltkamp 1994) was published in June 1994 and the second will be published early next quarter.

  - **August 31, 1994:** Complete Phase 3 surface monitoring work and provide a report.

  - **September 30, 1995:** Complete the surface moisture measuring development work and the in-tank demonstration test.

  - **September 30, 1996:** Initiate installation of surface moisture monitoring equipment if the demonstration test is successful and the need is warranted.

  - **September 30, 1997:** Complete installation of the surface moisture monitoring system, if warranted.

4.4.3 Preparation and Characterization of Ferrocyanide Waste Simulants

Ferrocyanide waste precipitates are being prepared and analyzed to determine the composition, physical properties, and chemical reaction properties of simulants that represent ferrocyanide waste stored in SSTs. The analytical results from these simulants, along with analyses of actual tank waste samples, waste tank monitoring, and waste modeling, provide information to characterize with a great deal of assurance safety concerns relating to the sludge in each of the ferrocyanide tanks.

Five waste simulants (without radioactive species) are being used to represent the variety of waste produced in the mid-1950s and stored in SSTs. Ferrocyanide waste produced at the Hanford U Plant is represented by U Plant 1 and U Plant 2 test mixtures. The U Plant 1 waste simulant represents 41 of 59 batches and the U Plant 2 simulant represents 9 of 59 batches of U Plant waste. The average U Plant batch volume was about 2,300,000 L. The other nine batches of U Plant waste are expected to have a ferrocyanide concentration between that of U Plant 1 and U Plant 2. A test mixture representing these batches will not be prepared and tested.

The In Farm flowsheet waste (in four C Farm tanks) is represented by In Farm 1 and In Farm 2 test mixtures. The In Farm 1 test mixture is representative of one batch (expected to have the greatest ferrocyanide concentration) of the 29 In Farm batches processed in the 1950s. In Farm 2 is representative of 11 intermediate ferrocyanide concentration batches of the 29 In Farm batches. An average-sized In Farm batch was approximately 1,500,000 L. It should also be noted that 6 of these 29 scavenging batches did not contain any ferrocyanide, but sodium sulfide was added to enhance precipitation of ^{60}Co.

A T Plant simulant was also prepared for testing to represent the six T Plant batches produced. An average sized T Plant batch was 2,098,000 L. The T Plant ferrocyanide sludge is stored in three TY Farm tanks.

Three main adjustments from the actual processes used in the 1950s were made in the laboratory scavenging preparation method to provide waste simulants representative of ferrocyanide sludges. These changes are as follows: (1) the solution concentrations were adjusted to include nitrite at a 1:3*M* ratio of nitrite/nitrate, to account for nitrite buildup over time in the waste by radiolysis of nitrate; (2) the waste simulants prepared for characterization do not contain radioactive isotopes present in actual waste, because of the difficulty in working with radioactive materials; and (3) the settled waste simulants from the laboratory scavenging process were typically centrifuged at a force of ~2,500 gravities to mimic an equivalent 30-year settling period.

The moisture content of ferrocyanide sludge is very important in the exothermic reaction behavior of ferrocyanide/nitrate-nitrite mixtures. Studies are underway to evaluate the moisture retention properties of ferrocyanide simulants as they relate to possible waste tank leaks, tank stabilization by pumping, and possible evaporation from exposed surfaces.

- **Progress During Reporting Period.** Three experiments have been conducted to determine the capability of simulant sludge to retain water against the pull of gravity, and thereby the material's resistance to dryout by drainage. The experiments are: (1) drainage from a 20-cm (8-in.)-long column of In Farm 2 simulant; (2) centrifugation of In Farm 2 simulant at various gravity (g) forces in a tube with an open-end fritted-glass filter; and (3) expulsion of supernatant from U Plant 1 simulant in a Tempe[4] cell with applied air pressure.

  In all three experiments, the loss of supernatant volume from the simulant samples was associated with an equal reduction of bulk volume. This occurred regardless of whether the supernatant was expelled by (1) natural drainage, (2) increased g force, or (3) applied air pressure. Because the samples remained liquid-saturated during shrinkage, the simulants lost water through a process called consolidation. Consolidation is the shrinking (collapse) of the volume of a porous medium by an applied load. In the draining small column, the load was produced by the sample's self-weight.

  Figure 4-1 shows the consolidation curve calculated for In Farm 2 simulant from centrifuge measurements at 1, 10, 20, 50, 100, and 2000 g's. A curve is fitted through the measured points to estimate values between actual measurements, and to make interpolation possible. Over a void ratio of 3.4 to nearly 1, In Farm simulant changed water content from 52 to 34 wt%.

[4]Trademark of Soil Moisture Equipment Corporation, Santa Barbara, California.

Figure 4-1. Consolidation Curve for In Farm 2 Simulant (Centrifuge Tests)

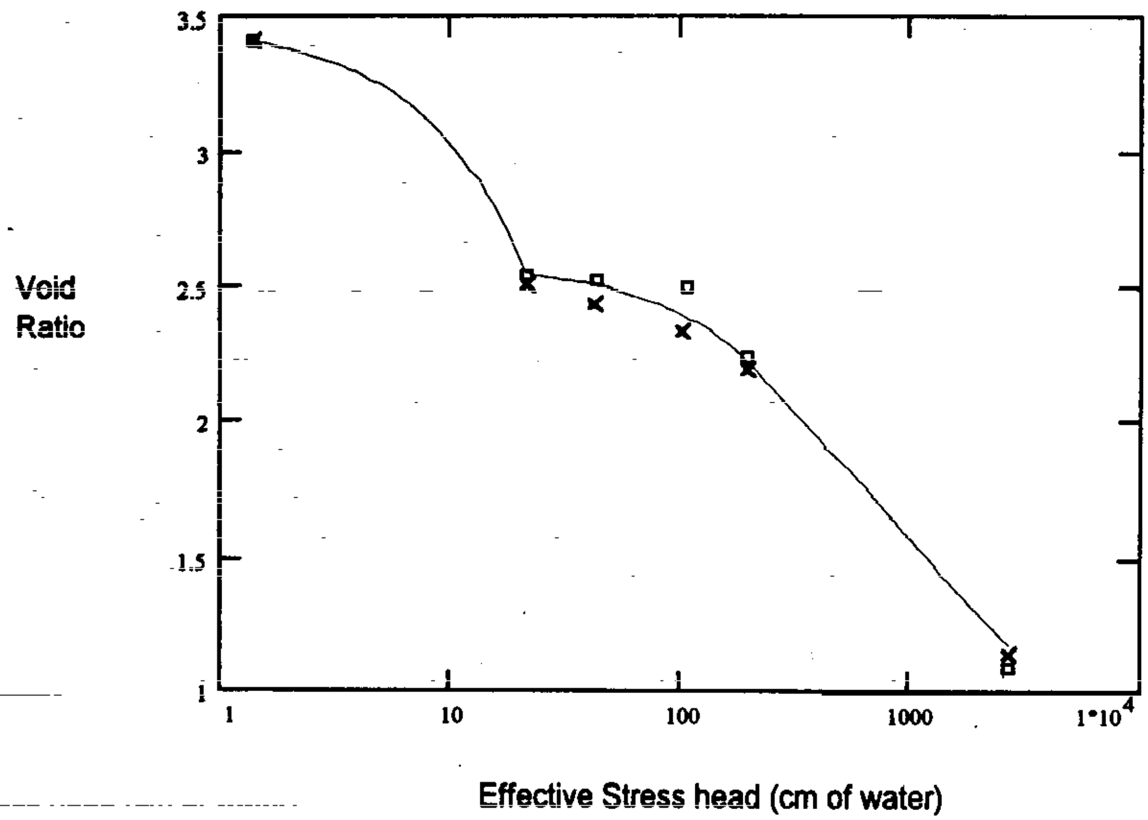
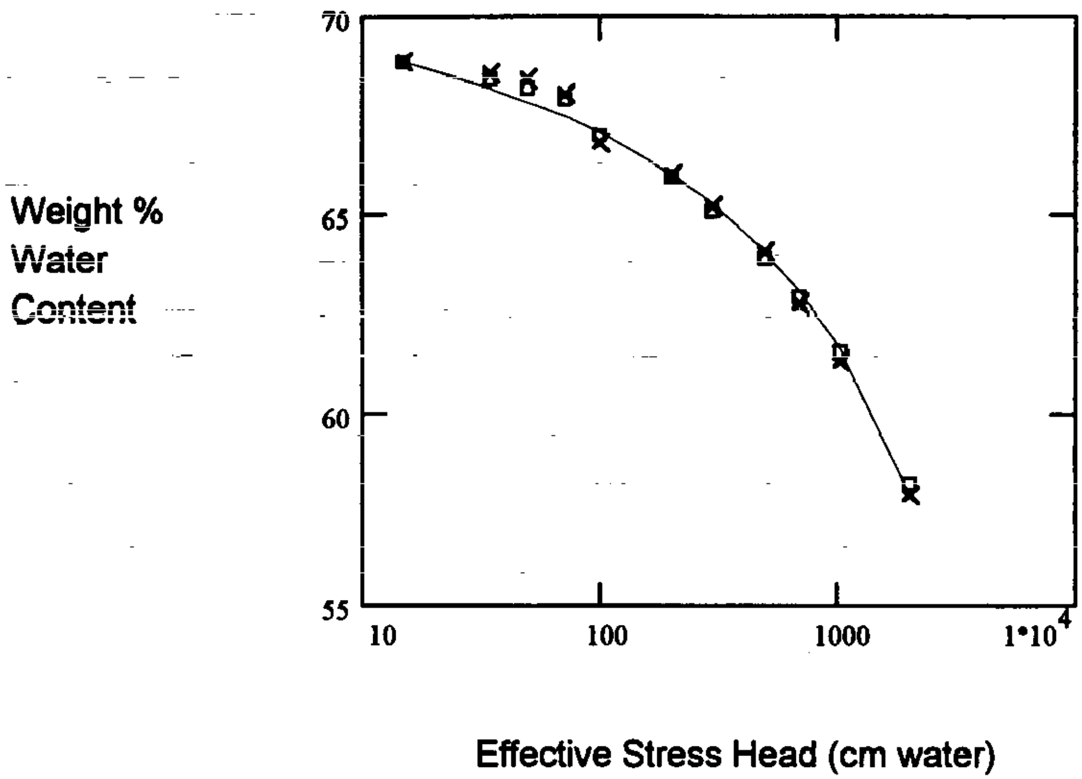


Figure 4-2 shows the consolidation curve obtained for U Plant 1 simulant. Results are presented directly in terms of wt% water instead of void ratio, by using a conversion. The actual curve in terms of void ratio is nearly linear on a logarithmic scale for effective stress head.

Figure 4-2. Consolidation Curve for U Plant 1 Simulant (Tempe™ Cell Tests)

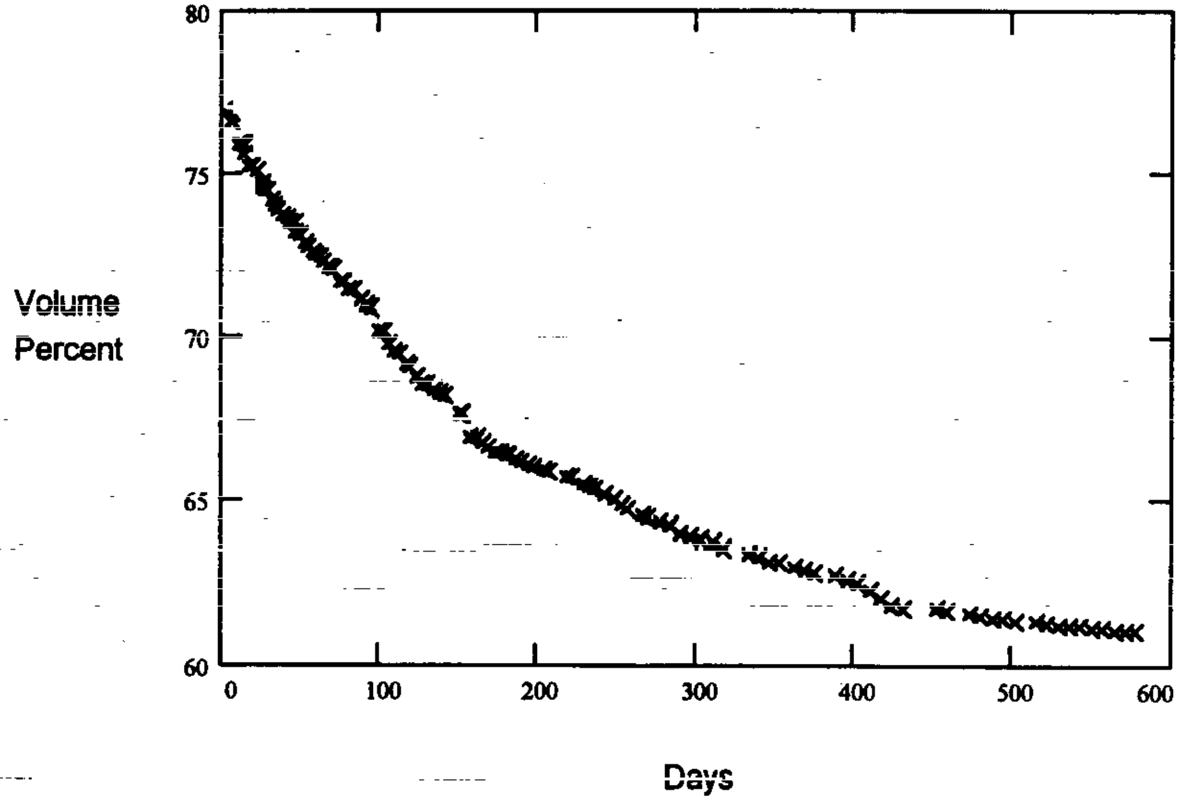


A small column of In Farm 2 simulant with an open bottom (sludge retained by screen and a porous filter paper) has drained for nearly two years. Originally, the experiment was set up to determine how dry a sludge sample would become if allowed to drain freely under gravity. The mass of the drained supernatant has been accumulated and measured over time. With this information and the presumption that the sample remains saturated as it consolidates, the volumetric liquid content in the column can be calculated (Figure 4-3).

In Figure 4-3, the volumetric liquid content appears to approach asymptotically a lower limit of 61 to 60 vol%. By using the consolidation characteristic of Figure 4-1, the average void ratio for attaining equilibrium with an open bottom is about 2.6, corresponding to 59 vol%. This indicates that drainage is now approaching completion. However, consolidation theory suggests that the drainage could continue indefinitely at a very diminished rate.

For the two years of drainage data obtained thus far, the exponential drainage model fits the trend well. However, in this small column experiment the change in void ratio or water content was not as large as might occur in a much larger size system that would have greater effective stress. To verify the model further, centrifugation tests were conducted on the In Farm 2 simulant contained in the small column.

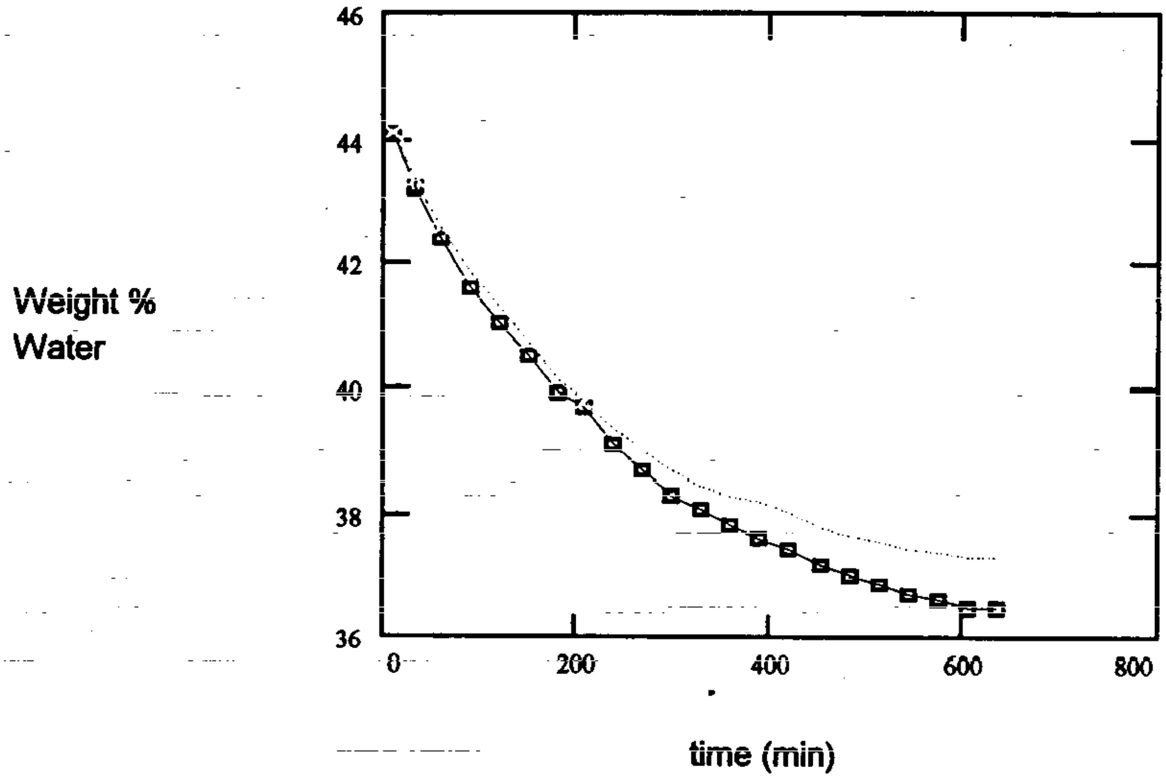
Figure 4-3. Volumetric Liquid Content of In Farm 2 Simulant (Small Column Test)



Samples were subjected to 500 g's that produced about 900 cm (354 in.) of effective stress head in the samples. Figure 4-4 shows the calculated wt% water content in the samples. The samples were driven from 45 to about 37 wt% water in only 10 hours. The lowest values correspond well with the consolidation curve in Figure 4-1, even though a different sample of In Farm 2 simulant was tested. This indicates that the simulants drain via consolidation regardless of the source of pressure (self weight, centrifugation, or applied air pressure).

The important observation from this work is that the simulants drain by the mechanism of consolidation, while remaining liquid saturated. The point at which simulants become de-saturated has not been discovered by the tests completed to date. Consolidation results in the greatest liquid loss at the bottom and the least reduction in water content at the surface. Therefore, the drainage behavior in sludge is opposite to that in a rigid porous medium, such as sand or saltcake. The simulants retain considerable water even though some amount can be drained by gravity. Direct measurement of the consolidation characteristic of actual waste is essential to predict the water retention capability of the sludge. Centrifugation is perhaps the fastest and most efficient way to test the hydraulic properties of sludges with only a small sample. Centrifugation also allows for testing over a greater range of effective stress in the least time.

Figure 4-4. Water Content of In Farm 2 Sample Subjected to 500 Gravities



- **Planned Work for Subsequent Months.** Modeling of the drainage properties of the simulants and centrifugation tests will continue. The effects of relative humidity on moisture content will be evaluated under geometric conditions representative of the SSTs.

  A report on the three methods used for drying the ferrocyanide waste simulants will be prepared and issued.

- **Problem Areas and Actions Taken.** None.

- **Milestone Status.**

  - **March 31, 1994:** Issue a report, available to the public, on the evaluation of the three waste simulant drying methods. Because of data interpretation difficulties, a decision was made to repeat some of the moisture analyses. The analyses were completed this quarter and a report will be published next quarter.

  - **May 31, 1994:** Issue a report, available to the public, on the chemical and physical properties of the T Plant ferrocyanide waste simulant. A report on testing of T Plant material was released ahead of schedule (Fauske and Jeppson 1994).

- **September 30, 1994:** Complete drainage tests on ferrocyanide waste simulants and issue a publicly available report on modeling and moisture retention by ferrocyanide sludge. This milestone remains on schedule.

- **September 30, 1994:** Issue a publicly available report on the effects of relative humidity on moisture retention in ferrocyanide waste. This milestone remains on schedule.

4.5 CHEMICAL REACTION STUDIES

"The schedule for the program on study of the chemical properties and explosive behavior of the waste in these tanks is indefinite and does not reflect the urgent need for a comprehensive and definitive assessment of the probability of a violent chemical reaction. The study should be extended to other metallic compounds of ferrocyanide that are known or believed to be present in the tanks, so that conclusions can be generalized as to the range of temperature and other properties needed for a rapid chemical reaction with sodium nitrate."

Chemical reaction studies on ferrocyanide waste simulants are being conducted by Westinghouse Hanford Company, Fauske and Associates, Inc. (FAI), PNL, and Los Alamos National Laboratory (LANL). Westinghouse Hanford Company and PNL have produced flowsheet simulant materials for testing and characterization. FAI is conducting adiabatic calorimetry and propagation tests on these same flowsheet materials. The test program at LANL was completed in FY 1993.

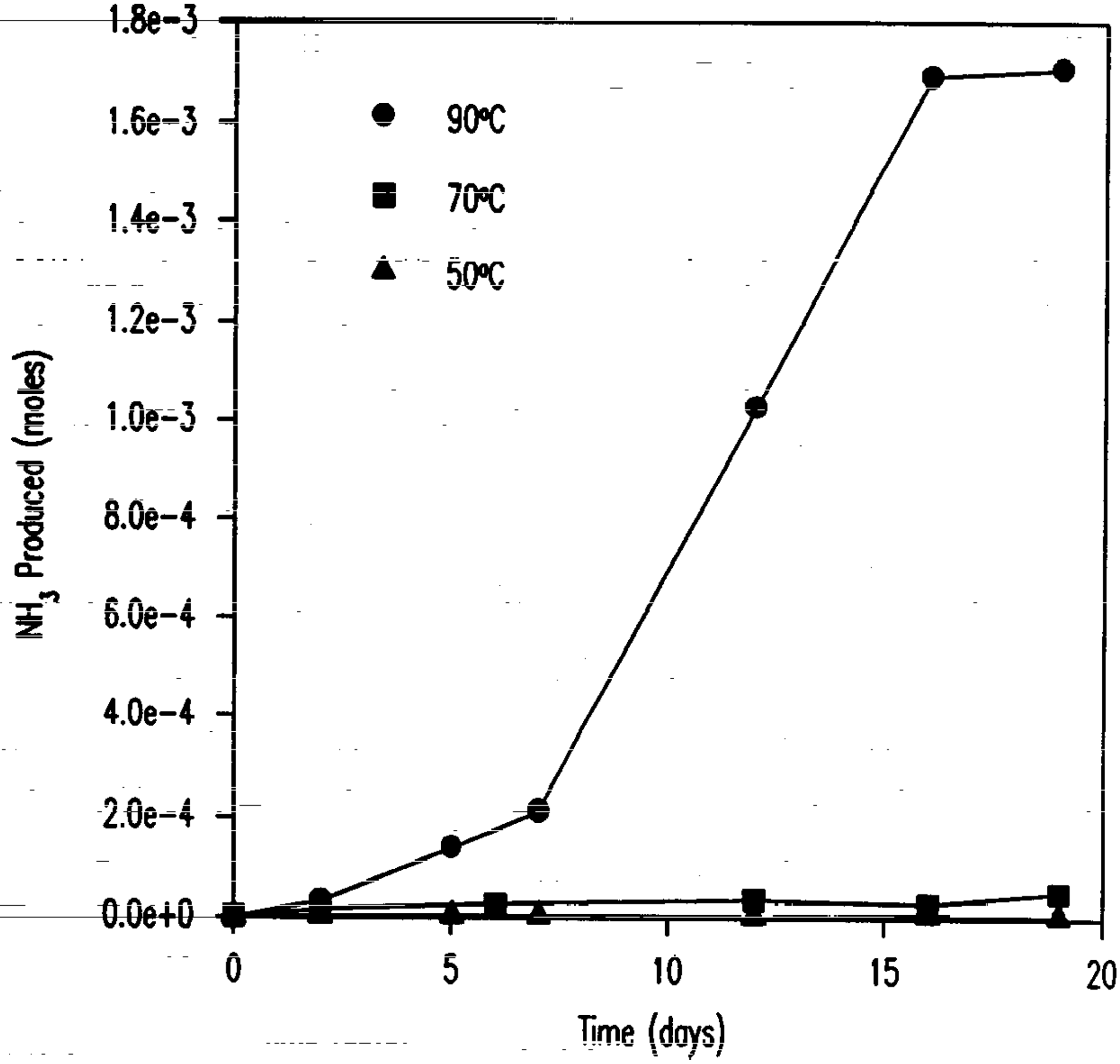
4.5.1 Chemical Reaction Studies at Pacific Northwest Laboratory

Chemical reaction studies are continuing at PNL using flowsheet simulant materials. Waste studies addressing DNFSB Recommendation 90-7.5 were conducted to determine: (1) aging effects of more than 35 years of storage in the tanks; (2) the speciation of cyanides found in the actual tank waste; (3) the solubility of sodium and cesium nickel ferrocyanides; and (4) possible microconvection mechanisms that may have allowed mixing of the ferrocyanide sludge with caustic solutions added to the tanks during tank operations.

- **Progress During Reporting Period.**

  Aging Studies. Additional work to determine the effect of temperature on the hydrolysis rate of In Farm 1 simulant in a gamma field was completed during the quarter. The experiments were conducted using 0.5 grams of In Farm 1 simulant in 2*M* sodium hydroxide, irradiated with gamma at 1×10^5 Rad/h and heated to 50, 70, and 90 °C, respectively. Samples were analyzed for ammonia and the results are shown in Figure 4-5. The rate of ammonia production (*M* in solution) is highly dependent on temperature. Ammonia production rate was more than an order of magnitude greater at 90 °C than at 60 °C.

Figure 4-5. Hydrolysis of In Farm 1 Simulant in 2*M* NaOH in a Gamma Field of 1 x 10^5 Rad/h at 50, 70, and 90 °C

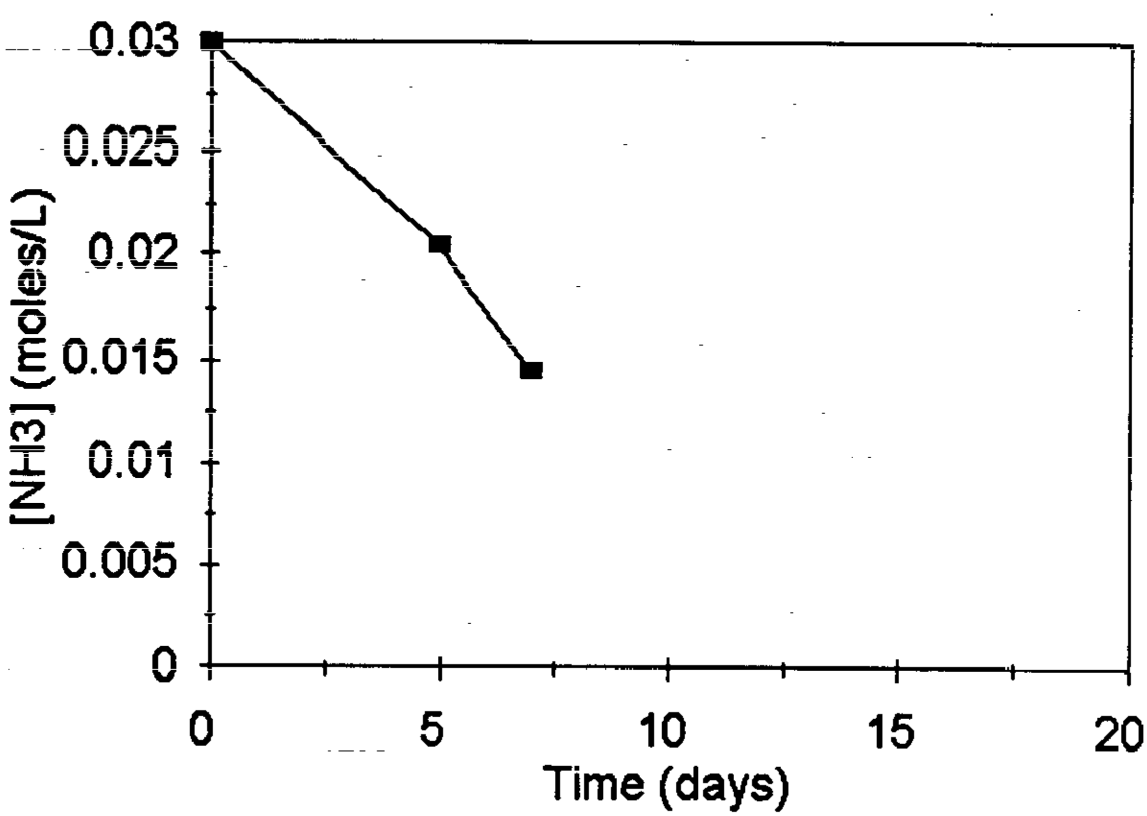


Ammonia production at 90 °C leveled off after 15 days; however, the amount of ammonia analyzed did not correspond to 100% hydrolysis (i.e., all of the cyanide groups were not hydrolyzed to ammonia). Two experiments were conducted to investigate this phenomenon. The first experiment examined whether ammonia was adsorbing on the stainless steel vessel walls. A known amount of ammonia was heated to 90 °C for two days, then cooled and sampled by the same technique used in the hydrolysis experiments. Results indicated that holdup on the stainless steel vessel walls is insignificant.

The second experiment was conducted to investigate the effect of gamma radiation on ammonia. Five vessels were charged with 2*M* sodium hydroxide containing nitrate and nitrite in the same proportion as contained in the In Farm 1 flowsheet material. Ammonium chloride was added to generate an initial ammonia concentration of 0.03*M*. The vessels were placed in the gamma field at a dose rate of 1×10^5 Rad/h and heated to 90 °C.

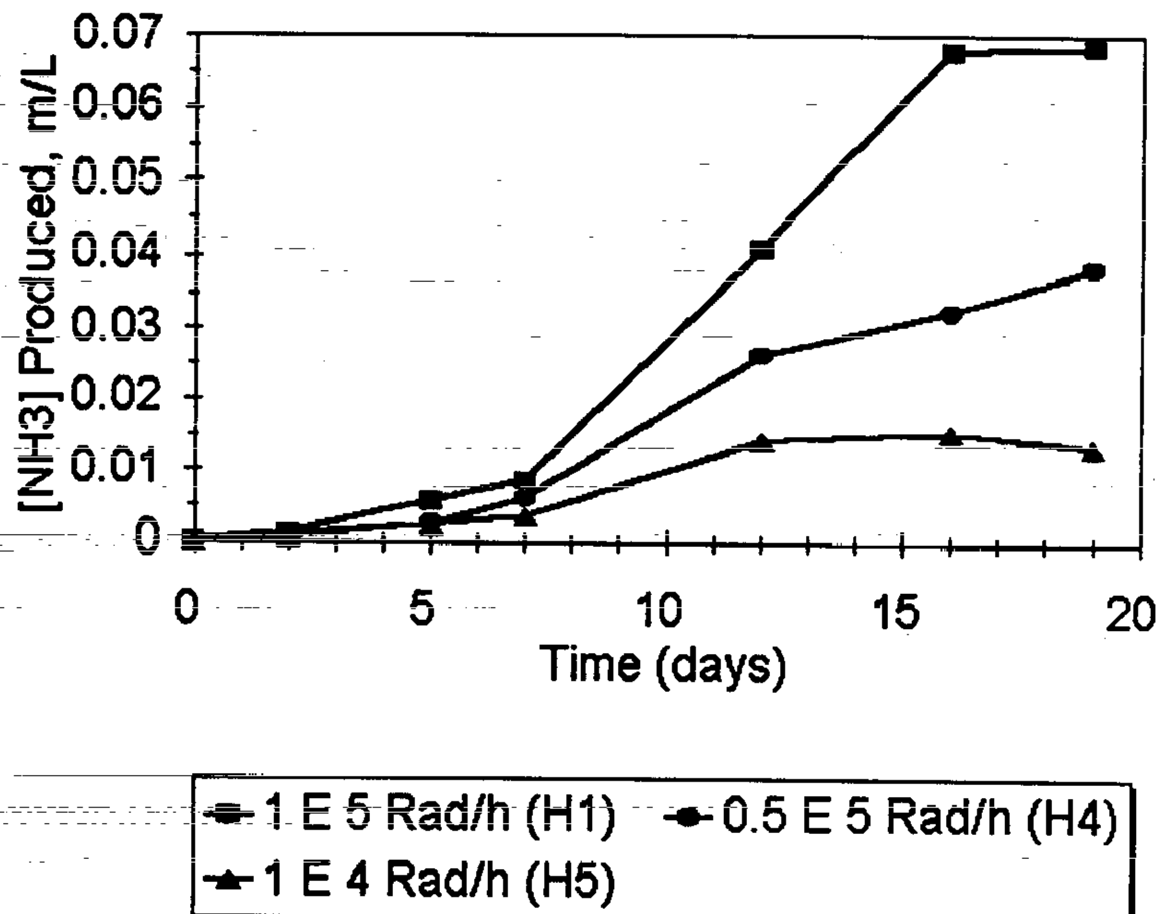
Figure 4-6 shows the results of the second experiment. Ammonia concentration decreases in a zero-order fashion (i.e., the plot of ammonia concentration versus time is linear), with a rate constant of 1.3×10^{-3}*M*/liter·day. This indicates that ammonia is destroyed as it is produced during the aging process. Therefore, complete hydrolysis of the cyanide groups to ammonia may have occurred, and the only accurate measure of the extent of aging may come from direct analysis of the tails (i.e., the aged simulants).

Figure 4-6. Ammonia Concentration as a Function of Time Under Gamma Irradiation



Experiments investigating the effect of gamma dose on the rate of ferrocyanide hydrolysis were also conducted this quarter. Figure 4-7 compares ammonia production from cyanide hydrolysis at different dose rates. Less ammonia is produced and at a slower rate as the gamma dose rate is decreased. Each curve shows a similar sigmoidal shape with about a seven-day induction period, a period of increased rate of ammonia production, followed by a decreasing or leveling off in concentration. At 1 x 10^4 Rad/h, the ammonia concentration appears to decrease after 19 days, indicating that the rate of ammonia production is slower than the rate of destruction at this dose rate.

Figure 4-7. Effect of Gamma Dose Rate on Ammonia Production by Hydrolysis



Total Integrated Dose Calculations. Because of the importance of dose in aging, an estimate of total integrated dose was calculated for each of the ferrocyanide tanks. Dose was calculated using an analytical spreadsheet model based on measured and calculated radiation dose rates. Gamma energy scans were available for the 10 Ferrocyanide Watch List tanks that contain LOWs. The direct measure of gamma energy was converted into a dose rate and then a total integrated dose. For the 10 Ferrocyanide Watch List tanks not containing LOWs, estimates of the radionuclide inventory from process flowsheets were used to calculate dose rates. The dose calculations for the non-LOW tanks are probably less accurate than the doses calculated for the tanks containing LOWs. Detailed explanations of the model and results are presented in Parra and Watson (1994). A summary of the average and maximum calculated integrated doses is presented in Table 4-1.

Table 4-1. Total Integrated Beta and Gamma Radiation Dose in Rads

Tank	LOW	Average (Rad)		Maximum (Rad)	
		Beta	Gamma	Beta	Gamma
241-BX-102	N	$1.7\ 10^{8}$	$3.4\ 10^{8}$	$7.3\ 10^{8}$	$1.4\ 10^{9}$
241-BX-106	N	$2.9\ 10^{8}$	$5.0\ 10^{8}$	$1.2\ 10^{9}$	$2.1\ 10^{9}$
241-BY-103	Y	$4.4\ 10^{7}$	$9.4\ 10^{7}$	$7.3\ 10^{7}$	$1.5\ 10^{8}$
241-BY-104	Y	$3.9\ 10^{7}$	$8.7\ 10^{7}$	$5.0\ 10^{7}$	$1.1\ 10^{8}$
241-BY-105	Y	$2.5\ 10^{7}$	$5.5\ 10^{7}$	$5.0\ 10^{7}$	$1.1\ 10^{8}$
241-BY-106	Y	$5.3\ 10^{7}$	$1.0\ 10^{8}$	$1.3\ 10^{8}$	$2.5\ 10^{8}$
241-BY-107	Y	$8.8\ 10^{7}$	$1.8\ 10^{8}$	$1.3\ 10^{8}$	$2.7\ 10^{8}$
241-BY-108	N	$4.2\ 10^{7}$	$9.0\ 10^{7}$	$1.1\ 10^{9}$	$3.7\ 10^{8}$
241-BY-110	Y	$4.1\ 10^{7}$	$9.4\ 10^{7}$	$7.6\ 10^{7}$	$1.7\ 10^{8}$
241-BY-111	Y	$1.8\ 10^{7}$	$3.8\ 10^{7}$	$4.0\ 10^{7}$	$8.3\ 10^{7}$
241-BY-112	Y	$2.6\ 10^{7}$	$5.0\ 10^{7}$	$9.2\ 10^{7}$	$1.8\ 10^{8}$
241-C-108	N	$2.6\ 10^{8}$	$4.3\ 10^{8}$	$1.1\ 10^{9}$	$1.8\ 10^{9}$
241-C-109	N	$2.9\ 10^{8}$	$5.3\ 10^{8}$	$1.2\ 10^{9}$	$2.2\ 10^{9}$
241-C-111	N	$2.3\ 10^{8}$	$4.4\ 10^{8}$	$9.5\ 10^{8}$	$1.8\ 10^{9}$
241-C-112	N	$1.2\ 10^{7}$	$2.4\ 10^{8}$	$5.1\ 10^{8}$	$9.9\ 10^{8}$
241-T-107	N	$7.9\ 10^{7}$	$1.8\ 10^{8}$	$3.3\ 10^{8}$	$7.5\ 10^{8}$
241-TX-118	Y	$1.4\ 10^{7}$	$2.9\ 10^{7}$	$2.8\ 10^{7}$	$5.6\ 10^{7}$

Tank	LOW	Average (Rad)		Maximum (Rad)	
		Beta	Gamma	Beta	Gamma
241-TY-101	N	9.7 10^7	2.0 10^8	4.1 10^8	8.2 10^8
241-TY-103	Y	5.2 10^7	9.9 10^7	1.4 10^7	2.7 10^8
241-TY-104	N	4.9 10^8	8.6 10^8	2.1 10^9	3.6 10^9

Tank 241-TY-104 had the highest estimated total integrated beta and gamma radiation doses. The maximum estimated integrated beta radiation dose value was 2.1 x 10^9 Rad, with a probable estimated average value of 4.9 x 10^8 Rad. The maximum estimated integrated gamma radiation dose was 3.6 x 10^9 Rad, with a probable estimated average value of 8.6 x 10^8 Rad.

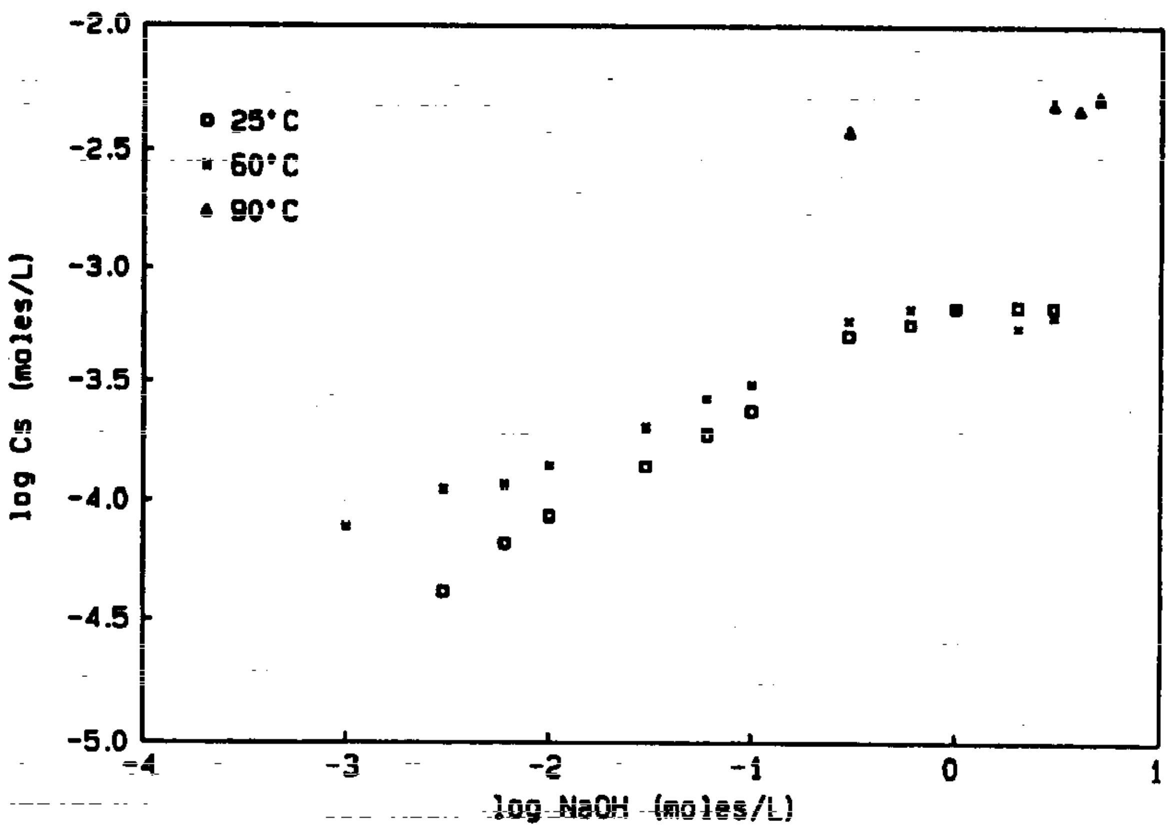
Cyanide Speciation. An FTIR spectrometer equipped with a remote detector was installed into a radiologically controlled laboratory this quarter. The instrument will be used for continued development of the FTIR cyanoferrate analytical technique with actual tank waste samples. Samples from tanks C-112 and C-109 were prepared for use in evaluation of the technique and further development of the speciation analysis. Work with the samples was halted in early April when an administrative hold was placed on all laboratory work within radioactive control areas of the 325 Building. The hold is in effect until a restart plan is approved by DOE. Restart is anticipated sometime next quarter; however, work requiring radioactive facilities is currently two months behind and will continue to slip until restart.

Development work on the ion chromatography (IC) speciation method continued during the quarter. Efforts were focused on assessing the influence of potential interferences, both organic and inorganic, when using the IC technique for the determination of cyanoferrate species. Solutions prepared eight months ago with organic and inorganic interferants revealed no aging effects. The concentration of the cyanide complex appears relatively stable in each of the solutions.

Microconvection Modeling. Microconvection modeling simulations using a new composite code that has capabilities for solving coupled fluid, heat, and mass transport problems were reported last quarter. Simulations using this new capability indicate that in a waste tank containing heat-producing radionuclides (e.g., ^{137}Cs), it is possible for the internal heat generation to establish a bifurcated flow field within the tank (Meacham et al. 1994). Convective mass transport is possible along the flow streamlines in the flow field. An initial analysis of how the thermal and chemical properties affect the transport of ^{137}Cs indicate that ^{137}Cs must exhibit retrograde solubility (i.e., decreasing solubility with increasing temperature) for this mechanism to contribute to "hot spot" formation. If ^{137}Cs exhibits increasing solubility with increasing temperature, the heat-generated mass transport will distribute the cesium more uniformly throughout the waste sludge.

Cesium/Sodium Nickel Ferrocyanide Solubility Studies. Solubility studies involving $Cs_2NiFe(CN)_6$ were expedited in order to address the issue of possible retrograde solubility of cesium raised by the microconvection modeling studies. Dicesium nickel ferrocyanide was prepared and suspended in sodium hydroxide solutions ranging in concentration from 0.001*M* to 5*M* at 25, 60, and 90 °C. The suspensions were sampled after five days, and the results are shown in Figure 4-8.

Figure 4-8. Solubility of $Cs_2NiFe(CN)_6$ in Caustic Solutions at 25, 60, and 90 °C



The solubility data indicate that at 25 °C the cesium concentration increases as the hydroxide concentration increases from 0.001*M* to about 1.0*M*. At hydroxide concentrations greater than 1.0*M*, the cesium concentration in solution appears to be constant. Cesium concentrations at 90 °C are about an order of magnitude higher than at 25 °C. These results provide a strong indication that cesium does not exhibit retrograde solubility.

- **Planned Work For Subsequent Months.** Aging experiments will be continued using In Farm flowsheet simulant. Knowledge of factors which impact the free cyanide concentration in solution are important to understanding the mechanism(s) involved in the hydrolysis reactions. Experiments will be conducted to determine factors that may have influenced hydrolysis rates under actual tank waste conditions.

  Cyanide speciation development, including IC methods and solution IR methods, will continue until the validated techniques and procedures can be routinely applied to samples in analytical laboratories at PNL and Westinghouse Hanford Company. The studies will include determination of interferences and possible corrections.

- **Problem Areas and Actions Taken.** All laboratory work has been halted within radioactive control areas in the 325 Building since early April. A draft restart plan was submitted to DOE and restart is anticipated sometime next quarter. The laboratory shutdown has affected completion of the work scope outlined in the FY 1994 test plans. Reports will be issued as scheduled in the milestones; however, some of work that was to be completed this FY in the cyanide speciation and cesium solubility tasks will be carried into next FY.

- **Milestone Status.**

  - **September 30, 1994:** Issue the final PNL report, cleared for public release, on FY 1994 hydrolysis and radiolysis aging experiments with ferrocyanide waste materials. This milestone remains on schedule.

  - **September 30, 1994:** Issue the final PNL report, cleared for public release, on solution IR and IC cyanoferrate speciation activities and application for routine measurements in the analytical laboratories. A report on FY 1994 activities will be issued, but a final report will not be prepared until all work is complete in FY 1995.

  - **September 30, 1994:** Issue a publicly available progress report on FY 1994 work on the solubility of sodium/cesium nickel ferrocyanide compounds, with recommendations on future work. This milestone remains on schedule.

  - **September 30, 1994:** Issue a PNL report, cleared for public release, on microconvection modeling and the effects projected to have occurred in the tank waste from this phenomenon during more than 35 years of storage. This milestone is on schedule.

- **September 30, 1994**: Issue a progress report, available to the public, on FY 1994 studies comparing chemical and physical parameters of ferrocyanide waste simulants with actual waste samples. The report will include recommendations on future work. This milestone remains on schedule.

- **September 30, 1995**: Issue the final PNL report integrating all Ferrocyanide Safety Program hydrolysis and radiolysis aging activities.

- **September 30, 1995**: Issue a final report, available to the public, on the solubility of sodium-cesium nickel ferrocyanide compounds under waste tank conditions.

- **September 30, 1995**: Issue a final report, available to the public, on studies comparing chemical and physical parameters of ferrocyanide waste simulants with actual tank waste samples.

4.5.2 Ferrocyanide Propagation Studies

Ferrocyanide adiabatic calorimetry and propagation tests are continuing at FAI under contract to Westinghouse Hanford Company. The results of these tests are being used to help determine if local regions within the ferrocyanide waste can ignite and burn to spread and involve additional waste from a potential ignition point. Propagation velocity is a key parameter in determining safety consequences of postulated burns, including a potential radioactivity release.

Because the composition of the waste in the storage tanks varies and is not known at all locations, ranges of material compositions have been tested. Present work is focused on the T Plant and the more reactive In Farm 1 simulants with varying amounts of sodium nickel ferrocyanide. Sludge produced by the In Farm flowsheet is stored in four C Farm tanks and represents about 26% of the total ferrocyanide used in the Hanford Site scavenging processes. Sludge produced by the T Plant flowsheet is stored in three TY Farm tanks and represents about 8% of the total ferrocyanide used during the Hanford Site scavenging processes. Adiabatic calorimeter tests have also been initiated to assess possible organic fuel contributions to energy releases during ferrocyanide reactions.

- Progress During Reporting Period. Efforts were directed this quarter at establishing criteria covering the onset of propagating reactions for all potential energetic materials (i.e., ferrocyanide, organic, etc.) contained in Hanford Site high-level waste tanks. Preliminary calculations at FAI indicate that a material containing no free or bound water (zero total water) must be capable of producing an energy release in excess of 500 Joules per gram (120 cal/g) to support a propagating reaction, irrespective of the fuel source (Fauske 1994). It was also noted that safe tank conditions could be corroborated with considerably less effort and expense by including the presence of water in the criterion.

- **Planned Work for Subsequent Months.** Define additional parametric and ferrocyanide/organic tests to be conducted and initiate these tests at FAI. Conduct dryout tests by simulating local heat generation in the sludge volume.

- **Milestone Status.**

  - **June 30, 1994:** Complete screening tests of In Farm 1 simulant at FAI by varying ferrocyanide and water compositions to define the empirical line that divides propagating and non-propagating mixtures on the triangle diagram (Postma et al. 1994). Tests were completed on schedule at FAI, and a report, cleared for public distribution, will be issued in September 1994.

  - **March 31, 1995:** Complete parametric aerosol tests at FAI (if required) that provide source terms for determining consequences of hypothetical ferrocyanide burns in a ferrocyanide tank.

  - **September 30, 1995:** Complete the ferrocyanide calorimetry and propagation test program at FAI as specified by Westinghouse Hanford Company and prepare reports, available for public release, that support resolution of the Ferrocyanide Safety Issue.

4.6 EMERGENCY RESPONSE PLANNING

"The Board had recommended 'that an action plan be developed for the measures to be taken to neutralize the conditions that may be signaled by alarms.' Two types of measures are implied: actions to respond to unexpected degradation of a tank or its contents, and actions to be taken if an explosion were to occur. Your implementation plan stated that 'the current contingency plans ... will be reviewed and revised if needed.' We do not consider that this proposed implementation of the Board's recommendation is adequately responsive. It is recommended that a written action plan founded on demonstrated principles be prepared as soon as possible, that would respond to indications of onset of abnormal temperatures or other unusual conditions in a ferrocyanide-bearing tank, to counter any perceived growth in hazard. A separate emergency plan should be formulated and instituted, covering measures that would be taken in event of an explosion or other event leading to an airborne release of radioactive material from the tanks, and that would protect personnel both on and off the Hanford Site. The Board believes that even though it is considered that the probability is small that such an event will occur, prudence dictates that steps be taken at this time to prepare the means to mitigate the unacceptable results that could ensue."

The *Action Plan for Response to Abnormal Conditions in Hanford Radioactive Waste Tanks Containing Ferrocyanide* was prepared in response to DNFSB Recommendation 90-7.6. The action plan describes the steps to be taken if a temperature increase trend above the tank temperature baseline is measured in any of the ferrocyanide tanks. The document was revised to include the monitoring criteria and responses for abnormal levels of flammable and toxic gases, as well as the reporting requirements, if established criteria are exceeded. The second revision of the plan was released this quarter (Fowler 1994).

The *Tank Farm Stabilization Plan For Emergency Response* (WHC 1991) was issued in March 1991. If a radioactive release from a ferrocyanide tank were to occur, it would be detected by one or more radiation monitoring systems. Significant airborne or ground surface releases that spread beyond the immediate tank or tank farm would be detected by the tank farm area radiation detectors. These monitoring systems are on all tank farms. An emergency involving an underground radioactive waste storage tank is a unique event with potentially serious consequences both onsite and offsite. The *Stabilization Plan* provides quick, preplanned actions that can be used to stabilize an emergency event at an underground radioactive waste storage tank.

All actions with respect to emergency planning, emergency event recognition, protective action recommendations, and emergency response procedures have been completed. Further revisions and occasional validation exercises will be accomplished as part of the normal Westinghouse Hanford Company and DOE emergency planning efforts. No further reporting on these issues is planned, and this part of DNFSB Recommendation 90-7.6 is considered complete and closed.

DOE considers this recommendation to be closed with the proviso that the abnormal conditions response plan and emergency plans are: (1) reviewed on a periodic basis; (2) revised and updated as required to incorporate any additional controls determined appropriate by the ongoing Waste Tank Safety Program investigations [e.g., the *Action Plan for Response to Abnormal Conditions in Hanford Site Radioactive Waste Tanks Containing Ferrocyanide* was updated and released this quarter (Fowler 1994)]; and (3) validation exercises for various waste tank accident scenarios are conducted (exercises for the tank farms are conducted every two years).

- **Progress During Reporting Period.** As noted in previous reports, all of the planned milestones for this task were completed.

- **Planned Work For Subsequent Months.** None planned.

- **Problem Areas and Action Taken.** None.

- **Milestone Status.** All milestones have been completed.

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5.0 PROGRAM SCHEDULES AND MILESTONES

Two sets of schedules (Figures 5-1 and 5-2) are presented in this section. The scope of some of the program activities has changed since the FY 1992 program plan (Cash and Dukelow 1992) and the revised implementation plan (Borsheim et al. 1992) were released, and progress should be tracked against the schedules presented here. These are the schedules provided in the ferrocyanide program plan (Borsheim et al. 1994) in March 1994.

The first set of schedules reviews milestones for FY 1991 through FY 1994; these have been statused through June 30, 1994. A status line was drawn showing the progress completed on each activity. Actions that have started or been completed are indicated by triangles that are filled in. Work indicated by open triangles has either not started or has not been completed. Diamonds indicate a TPA milestone.

The second set of schedules reviews out-year milestones for FY 1994 through the expected end of the program in FY 1997. The sequence and anticipated completion dates of the major milestones leading to Safety Issue resolution are presented.

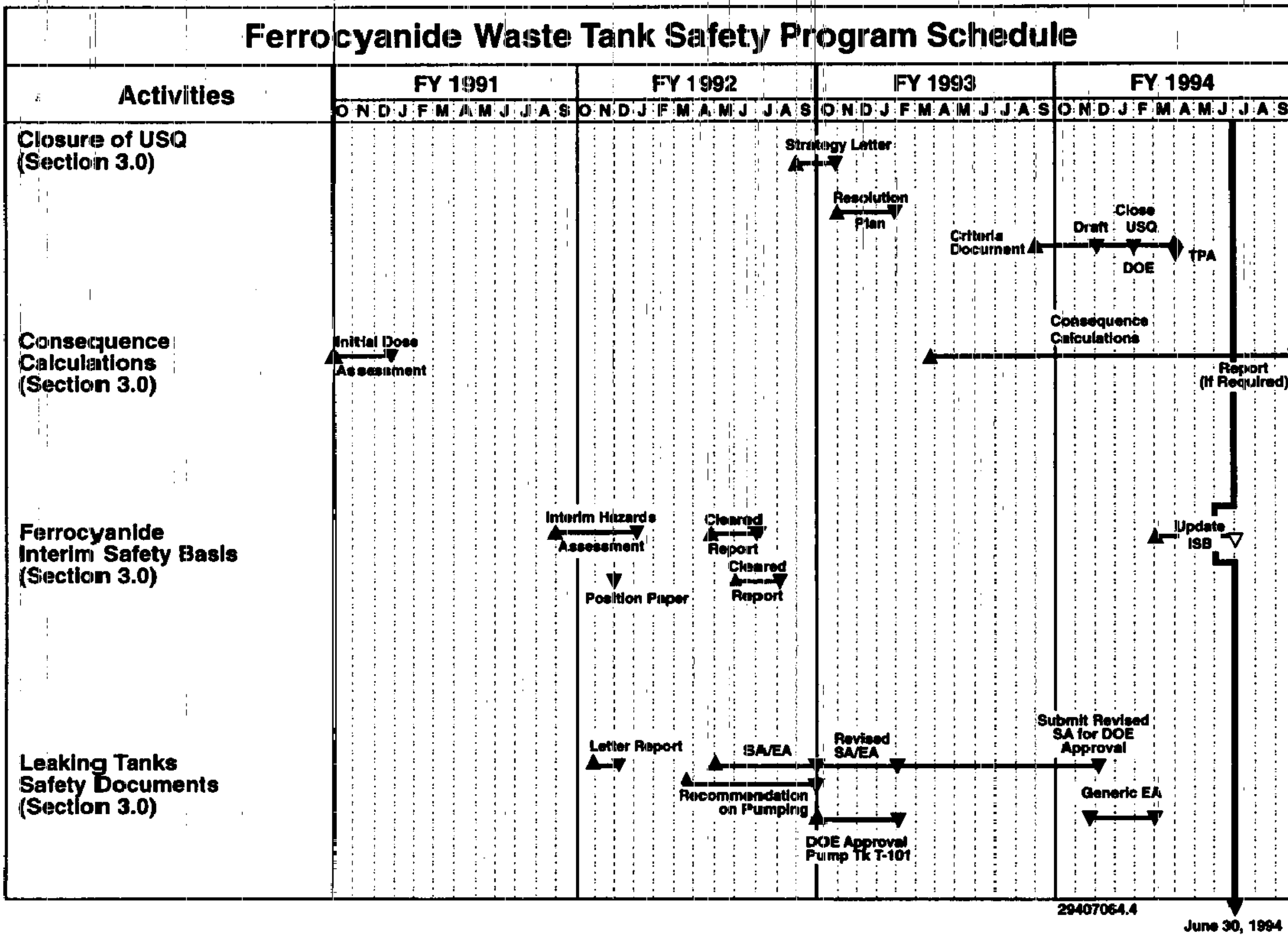

Figure 5-1. Ferrocyanide Waste Tank Safety Schedule. (Sheet 1 of 4)

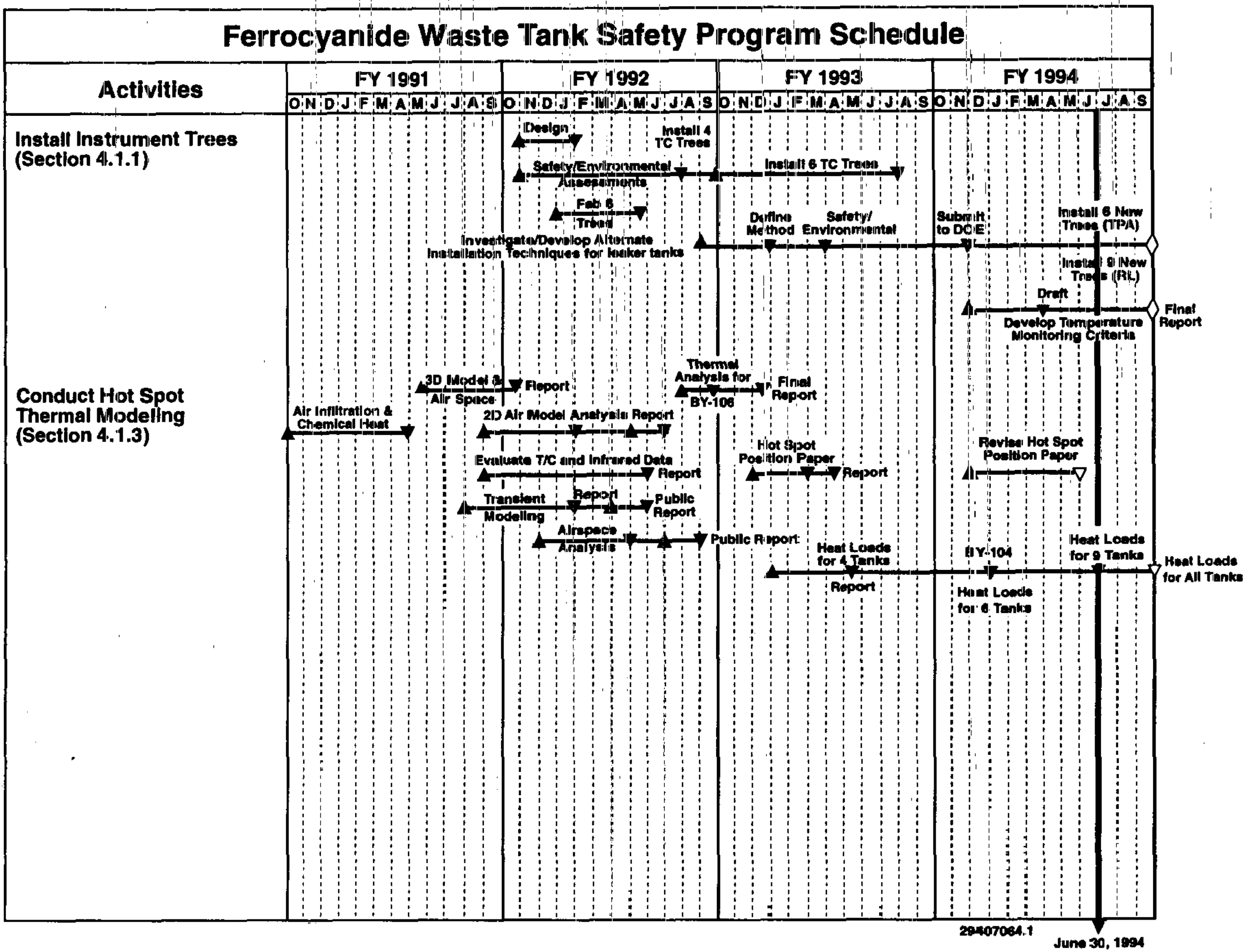

Figure 5-1. Ferrocyanide Waste Tank Safety Schedule. (Sheet 2 of 4)

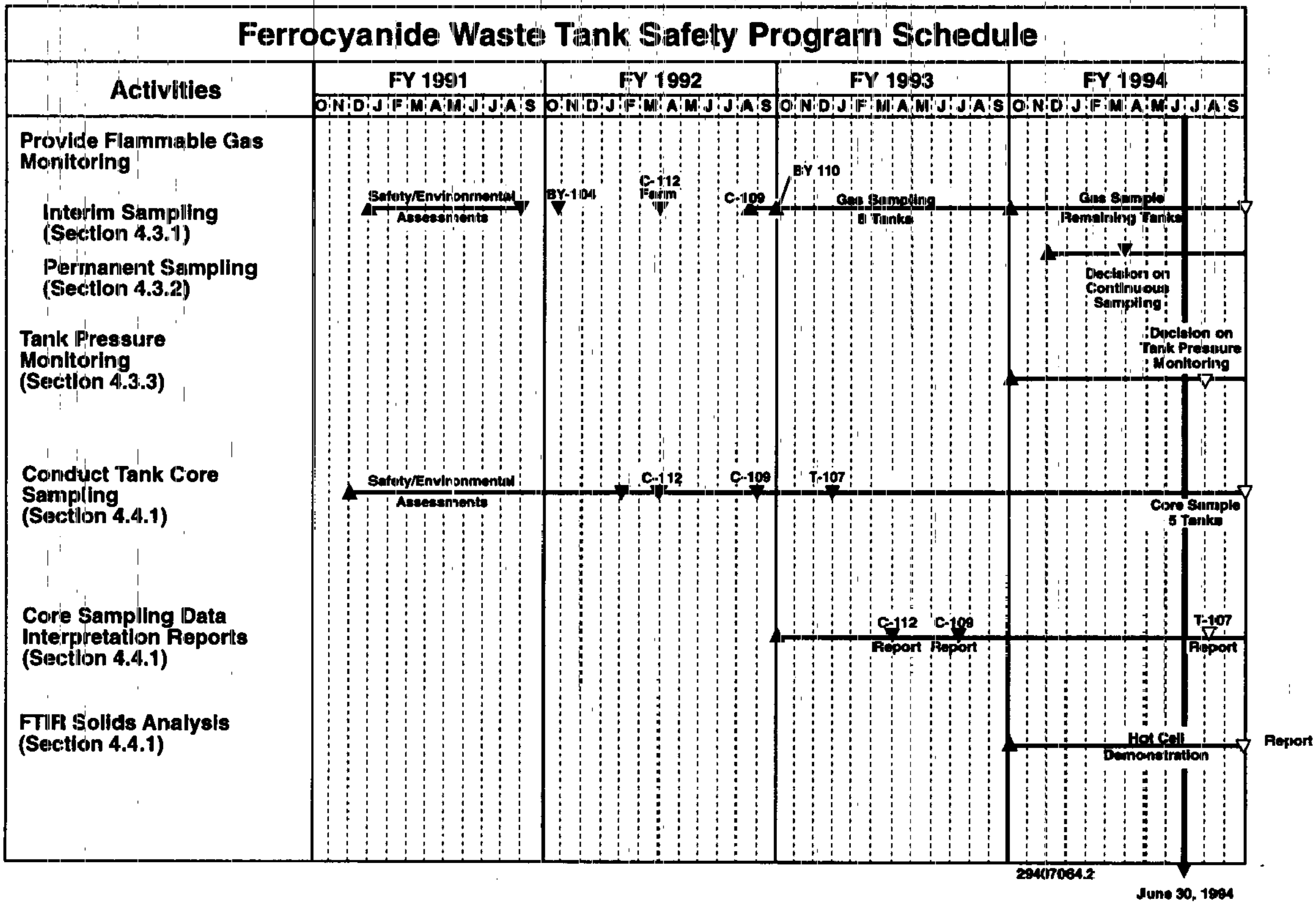

Figure 5-1. Ferrocyanide Waste Tank Safety Schedule. (Sheet 3 of 4)

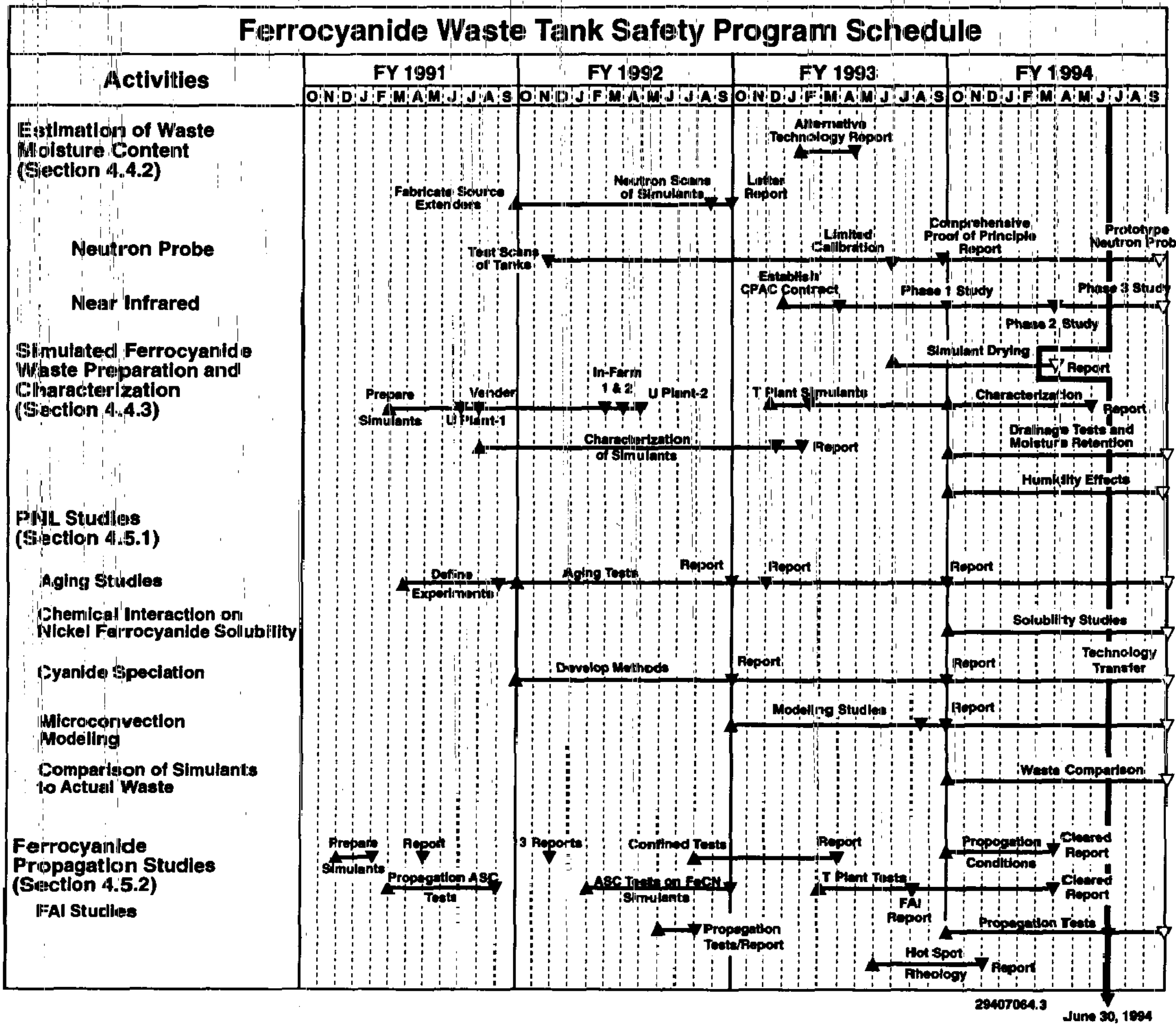

Figure 5-1. Ferrocyanide Waste Tank Safety Schedule. (Sheet 4 of 4)

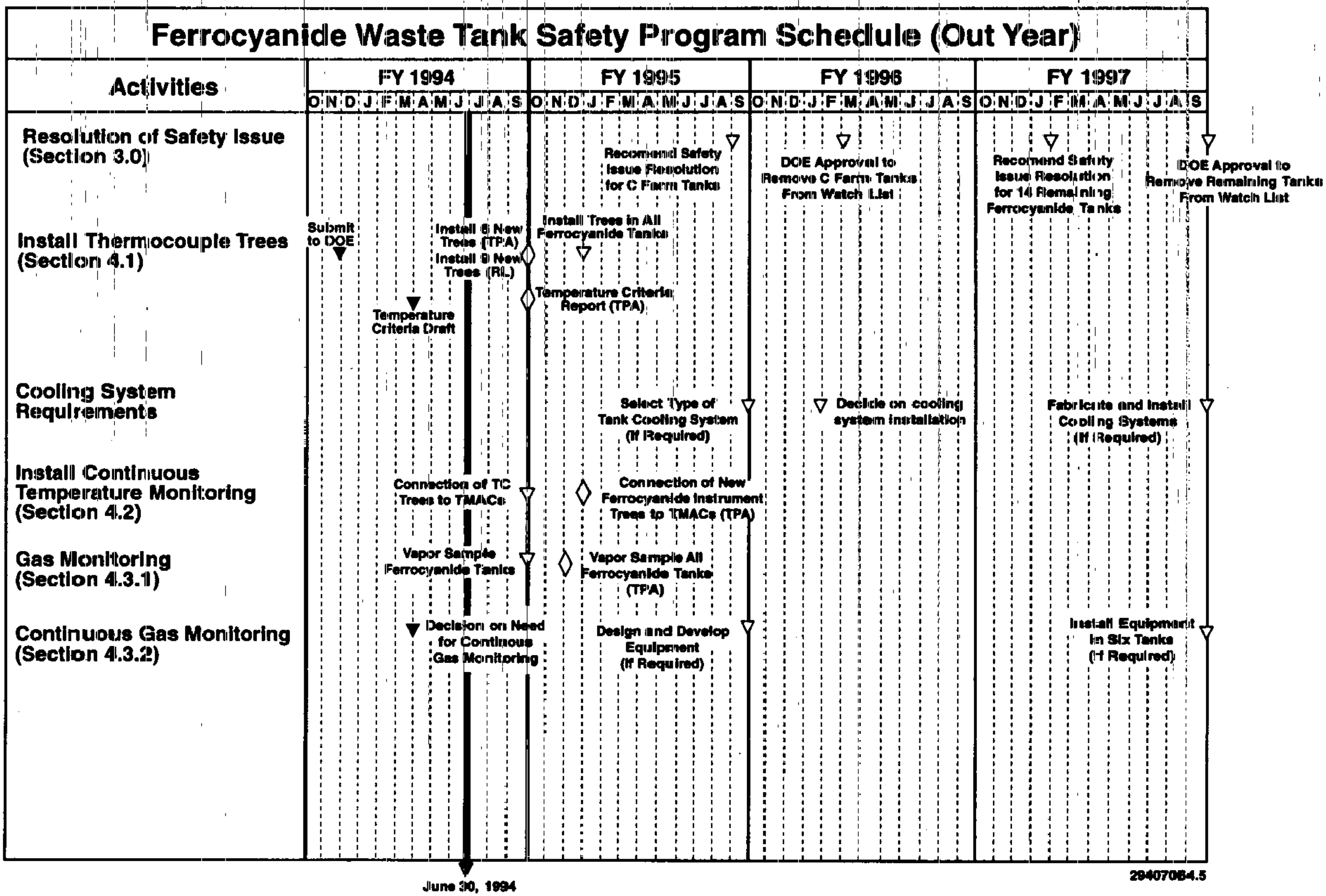

Figure 5-2. Ferrocyanide Waste Tank Safety Schedule (Out Year). (Sheet 1 of 2)

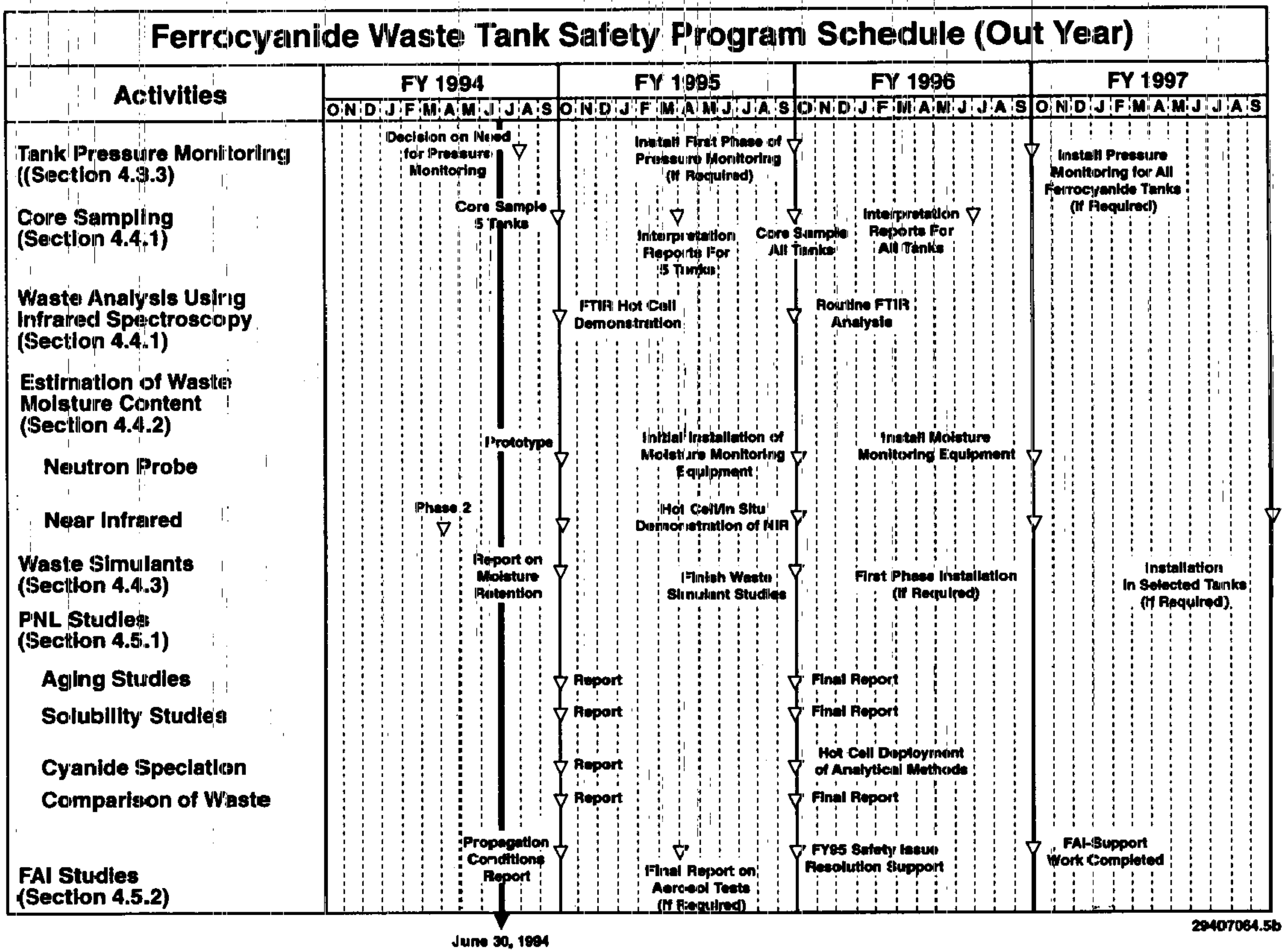

Figure 5-2. Ferrocyanide Waste Tank Safety Program Schedule (Out Year). (Sheet 2 of 2)

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APPENDIX A

FERROCYANIDE TANKS

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Table A-1. Summary of Contents and Status of Ferrocyanide Tanks[a].

Tank	Total waste volume (1,000 gal)	FeCN[b] (1,000 g-mole)	Heat load (Btu/h)[c]	Maximum temp. (°C)	(°F)	Status of tanks[d]
BX-102	96	<1	2,800	19	66	IS; AL
BX-106	46	<1	2,500	19 19[e]	66 66	NS; Sound
BY-103	400	66	5,500	27	80	NS; AL
BY-104	406	83	8,700	52 46[e]	126 114	IS; Sound
BY-105	503	36	8,700	45 49	113 120	NS; AL
BY-106	642	70	10,100	53	128	NS; AL
BY-107	266	42	8,900	36 --[f]	97 --	IS; AL
BY-108	228	58	9,200	42	108	IS; AL
BY-110	398	71	6,900	48 42[e]	118 107	IS; Sound
BY-111	459	6	5,500	31[g] 28[e]	87 83	IS; Sound
BY-112	291	2	6,100	28[g] 31[e]	82 88	IS; Sound
C-108	66	25	6,000	23 24[e]	73 75	IS; Sound
C-109	66	6.8[h]	7,000	27 26[e]	80 78	IS; Sound
C-111	57	33	6,400	23	73	IS; AL
C-112	104	11.5[h]	7,500	27 27[e]	80 81	IS; Sound
T-107	180	5	3,000	19	67	NS; AL
TX-118	347	<3	4,600	24 --[f]	75 --	IS; Sound

Table A-1. Summary of Contents and Status of Ferrocyanide Tanks[a].

Tank	Total waste volume (1,000 gal)	FeCN[b] (1,000 g-mole)	Heat load (Btu/h)[c]	Maximum temp. (°C)	Maximum temp. (°F)	Status of tanks[d]
TY-101	118	23	3,100	19	67	IS; AL
TY-103	162	28	4,000	20	68	IS; AL
TY-104	46	12	3,000	19	67	IS; AL

[a] Reflects removal of four ferrocyanide tanks from Watch List in July 1993. Tank information and temperature data as of June 1994.
[b] Inventories from Borsheim and Simpson (1991).
[c] Heat load values from Table 7-1 in Crowe et al. (1993).
[d] IS - Interim Stabilized Tank; NS - Not Stabilized; AL - Assumed Leaker Tank; Sound - Non-Leaking Tank.
[e] Readings from new instrument trees; tank 241-BY-105 already had two trees.
[f] Readings have not yet been taken on this new instrument tree.
[g] Reading from TC element in LOW.
[h] Calculated as ferrocyanide $[Fe(CN)_6^{4-}]$ based on the total cyanide values reported in Simpson et al. (1993a, 1993b).

Table A-2. Ferrocyanide Tank Vapor Sampling Summary

Tank	Date Sampled	Flamm (% LEL)	Organic Vapor (ppm)	Ammonia (ppm)	HCN/CN (ppm)	Nitrous Gas (ppm)
BX-106	06/17/93	<1	12	18	<2	<0.5
BY-103	05/05/94	<1	1.2	25	<2	<0.5
BY-104	10/16/91-10/30/91 04/22/94	1 <1	37 26	250 200	<2 NA[a]	>10 <0.5
BY-105	05/09/94	<1	4.9	40	NA	NA
BY-106	05/04/94	<1	5.7	60	NA	NA
BY-107	03/25/94	3 - 4	67	97	NA	NA
BY-108	03/28/94	1	97	700[b]	NA	<0.5
BY-110	09/27/92	<1	350	612[b]	<2	<0.5
BY-111	03/25/93 05/11/94	<1 <1	6.3 8.9	10 60	<2 NA	<0.5 NA
BY-112	03/26/93	<1	5.9	10	<2	<0.5
C-108	07/23/93	<1	1.2	<2	<2	<0.5
C-109	08/26/92 06/23/94	<1 <1	NA 1.0	<5 4	<2 NA	<0.5 NA
C-111	08/11/93	<1	<0.2	<2	<2	<0.5
C-112	03/09/92 - 03/18/92 06/24/94	<1 <1	<0.2 <0.2	<5 4	<2 NA	<2 NA
T-107	10/22/92	<1	24	203	<2	<0.5
TX-118	07/28/93	<1	0.3	10	<2	0.5

[a]NA = Not Available.
[b]Approximation because concentration exceeded calibration range.

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APPENDIX B

METRIC CONVERSION CHART

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Table B-1. Metric Conversion Chart.

Into Metric			Out of Metric		
If You Know	Multiply By	To Get	If You Know	Multiply By	To Get
Length			Length		
in.	2.54	cm	mm	0.04	in.
ft	30.48	cm	cm	0.4	in.
Mass (weight)			Mass (weight)		
lb	0.453515	kg	kg	2.2	lb
Volume			Volume		
gal	3.78541	L	L	0.264172	gal
Temperature			Temperature		
Fahrenheit (°F)	Subtract 32 then multiply by 0.55555...	Celsius (°C)	Celsius (°C)	Multiply by 1.8, then add 32	Fahrenheit (°F)

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